Solidification

Solidification

Solidification or freezing is a phase transition, in which a liquid turns into a solid when its temperature is lowered below its freezing point. If the solidification is very rapid, then the melt may become a frozen melt and the structure is very similar to what is called glass (i.e. amorphous structure). For crystallization of materials, slow solidification is a precondition. When temperature of liquid is lowered enough, the molecular velocity decrease and forms a cluster of atoms. If the radius is higher than certain critical radius, it forms nucleus.

In solidification process:

i) The energy of liquid is less than that of solid above the melting point. Hence liquid is stable above the melting point.

ii) The energy of solid is less than that of liquid below the melting point. Hence solid is stable below the melting point.

iii) At melting point, liquid gets converted into solid

Nucleation

In the context of solidification, the term **nucleation** refers to the formation of the first nanocrystallites from molten material. For example, as water begins to freeze, nanocrystals, known as **nuclei**, form first. In a broader sense, the term nucleation refers to the initial stage of formation of one phase from another phase. When a vapor condenses into liquid, the nanoscale sized drops of liquid that appear when the condensation begins are referred to as nuclei. Later, we will also see that there are many systems in which the nuclei of a solid (β) will form from a second solid material (α) (i.e., α-to-β phase transformation)

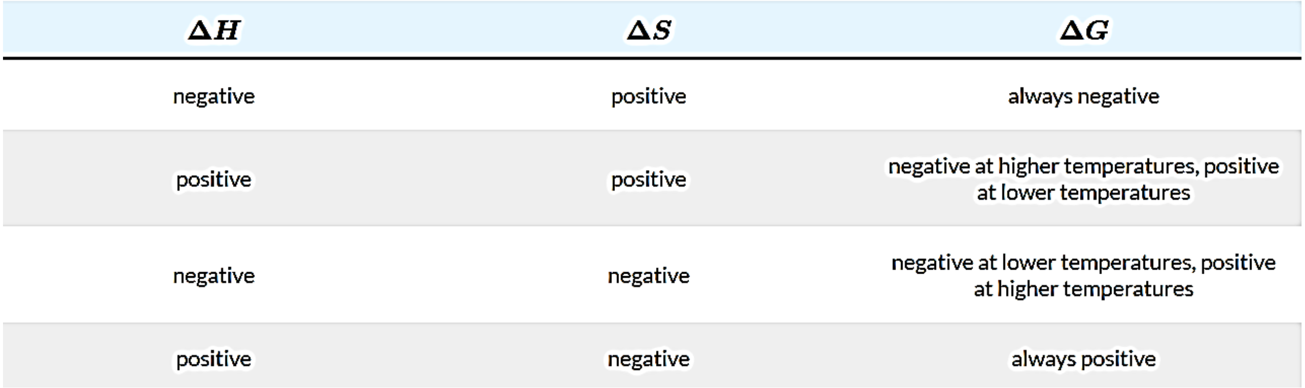
Homogeneous Nucleation

Homogeneous nucleation occurs in a liquid when the melt itself provides the atoms to form nuclei. In this case liquid metal is cooled below its equilibrium freezing temp to a sufficient degree. In this process, many homogeneous nuclei are created by slow-moving atoms bonding together. Homogeneous nucleation usually requires a considerable amount of undercooling which may be as much as several hundred degree centigrade for some metals. For a nucleus to be stable so that it can grow into a crystal, it must reach a critical size. A cluster of atoms bonded together which is less than the critical size called an embryo and which is larger than the critical size is called a nucleus. Embryo is highly unstable therefore continuously being formed and re-dissolved in the molten metal due to agitation of the atoms.

The Gibbs Free Energy *or Gibbs energy or Gibbs function or simply the free enthalpy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy* ($\Delta G^o = \Delta H^o - T\Delta S^o$; *J in SI units) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system.*

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta$H indicates that the reaction is exothermic and a $+\Delta$H means the reaction is endothermic. For entropy, $+\Delta$S means the entropy is increasing and the system is becoming more disordered. A $-\Delta$S means that entropy is decreasing and the system is becoming less disordered

$$\Delta G^o = \Delta H^o - T\Delta S^o$$



ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

The Helmholtz Free Energy *is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume (isothermal, isochoric).*

Energies involved in homogeneous nucleation

Let T_m = Melting point of specimen

T = Temperature of the melt

$\Delta T = T_m - T$ = amount of cooling

We know the change in the bulk volume free energy ΔG_v of 1cm^3 of liquid melt from the equation

$$\Delta G_v = G^s - G^l = H^s - H^l - T(S^s - S^l)$$

$$\Delta G_v = \Delta G = \Delta H - T(\Delta S) \qquad (1)$$

For spontaneous solidification, let,

$$H^s - H^l \approx -\Delta H_f \qquad [\, f \rightarrow \text{fusion} \,]$$

$$S^s - S^l \approx -\Delta S_f = -\frac{\Delta H_f}{T_m} \qquad \left[\begin{matrix}\text{Change in entropy} \\ \text{in fusion}\end{matrix}\right]$$

Putting in equation 1,

$$\Delta G_v = -\Delta H_f - T\left(-\frac{\Delta H_f}{T_m}\right)$$

$$= -\Delta H_f - \frac{T}{T_m}\left(-\Delta H_f\right)$$

$$= -\Delta H_f\left[\frac{T_m - T}{T_m}\right]$$

$$= -\frac{\Delta H_f}{T_m}\Delta T$$

$$= \alpha\Delta T$$

In homogeneous nucleation of a solidifying pure metal, two kinds of energy changes must be considered:
(i) the volume (or bulk) free energy released by the liquid-to-solid transformation and
(ii) the surface energy required to form the new solid surface of the solidified particles (retarding energy)

If ΔG_v is the change in free energy between the liquid and solid per unit volume of metal then the free energy change for a spherical nucleus of radius r is $\frac{4}{3}\pi r^3\Delta G_v$. This is the driving energy for liquid-to-solid transformation.

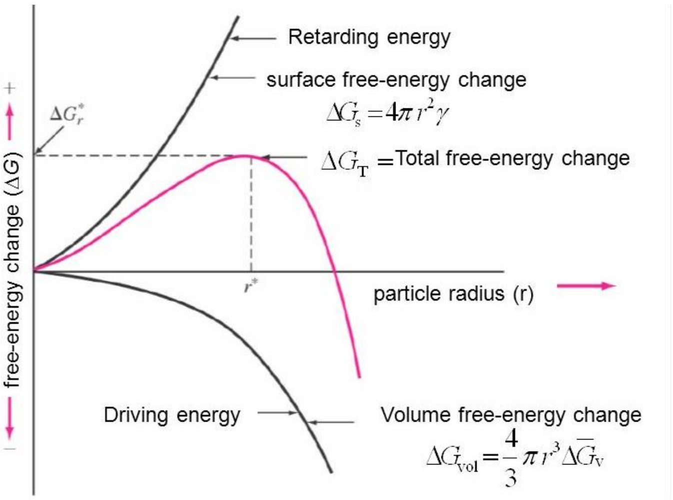


Fig. 1: Schematic diagram of energies involved in homogeneous nucleation.

However, the energy required to form the surface of these particles act as an opposing energy to the formation of embryos and nuclei. The energy needed to create a surface for these spherical particles, ΔG_s, is equal to the specific surface free energy of the particle, γ, times the area of the surface of the sphere, or $\Delta G_s = 4\pi r^2\gamma$. This retarding free energy for the formation of solid particles is shown in fig.1 by an upward curve in the positive upper half of the figure. The total free energy associated with the formation of an embryo of nucleus, which is sum of the volume free-energy and surface free-energy. The total change in free energy

(2)

$$\Delta G_T = \frac{4}{3}\pi r^3\Delta G_v + 4\pi r^2\gamma$$

For critical size of nucleus differentiation w.r.to r,

$$\frac{\partial\Delta G_T}{\partial \mathrm{r}} = 4\pi r^2\Delta G_v + 4\pi\gamma.2r = 0$$

$$\Rightarrow 4\pi r^2\Delta G_v = -4\pi\gamma.2r$$

$$\Rightarrow r = -\frac{2\gamma}{\Delta G_v} = r^* \tag{3}$$

Putting this value of r in equation 2

$$\Delta G_T{}^* = \frac{4}{3}\pi\left(-\frac{2\gamma}{\Delta G_v}\right)^3 \Delta G_v + 4\pi\left(-\frac{2\gamma}{\Delta G_v}\right)^2 \gamma$$

$$\Delta G_T{}^* = -\frac{32\pi\gamma^3}{3(\Delta G_v)^2} + \frac{16\pi\gamma^3}{(\Delta G_v)^2}$$

$$= \frac{\pi\gamma^3}{(\Delta G_v)^2}\left(16 - \frac{32}{3}\right)$$

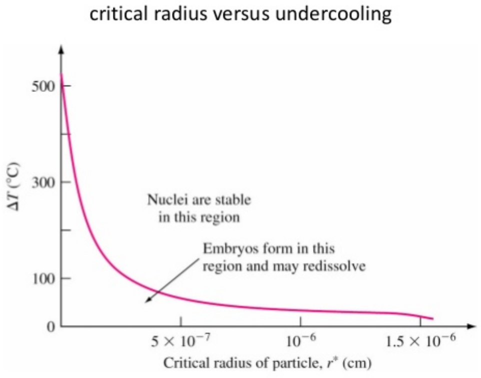
$$= \frac{16\pi\gamma^3}{3(\alpha\Delta T)^2} \qquad [As \quad \Delta G_v = \alpha\Delta T]$$

Again

$$r^* = -\frac{2\gamma}{\alpha\Delta T} = \frac{2\gamma T_m}{\Delta T \Delta H_f} \qquad \left[As \quad \alpha = -\frac{\Delta H_f}{T_m}\right]$$

Critical size versus undercooling:

Greater the degree of undercooling below the equilibrium melting temperature, the greater the change in volume free energy ΔG_v. However, the change in free energy due to the surface energy ΔG_s does not change much with temperature. Thus, the critical size is determined mainly by ΔG_v. Near the freezing temperature, the critical size must be infinite since ΔT approaches zero. As the amount of undercooling increases, the critical nucleus size decreases.



Critical Size of Nucleus: The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.

Problem 1: (a): Calculate the critical radius (in centimeters) of a homogeneous nucleus that forms when pure liquid copper solidifies. Assume ΔT (undercooling) = 0.2 T_m. $\gamma = 177 \times 10^{-7}\ joul/cm^2$, T_m =1083°C, ΔH_f=1826 $joul/cm^3$.

(b) Calculate the number of atoms in the critical sized nucleus at this undercooling

Solution: (a)

We know,

$$r^* = -\frac{2\gamma}{\alpha\Delta T} = \frac{2\gamma T_m}{\Delta T \Delta H_f}$$

$$= \frac{2 \times 177 \times 10^{-7} \times T_m}{0.2\,Tm \times 1826}$$

$$= 9.693 \times 10^{-8} cm$$

(b) Volume of the critical-sized nucleus = $\frac{4}{3}\pi r^{*3} = \frac{4}{3} \times 3.1416 \times (9.693 \times 10^{-8})^3$

$$= 3.815 \times 10^{-21} cm^3$$

Volume of the unit cell of Cu (a=0.361nm) = a^3 = $(3.61 \times 10^{-8})^3 cm^3 = 4.70 \times 10^{-23} cm^3$

Since there are four atoms per FCC unit cell,

Volume/atom= $\frac{4.70\times10^{-23} cm^3}{4} = 1.175 \times 10^{-23} cm^3$

Thus, the number of atoms per homogeneous critical nucleus is

$$\frac{Volume\ of\ the\ nucleus}{Volume/atom} = \frac{3.815 \times 10^{-21} cm^3}{1.175 \times 10^{-23} cm^3} = 325\ atoms.$$

Problem 2: (a): Calculate the critical radius (in centimeters) of a homogeneous nucleus that forms when pure liquid nickel (FCC structure) solidifies. Assume ΔT (undercooling) = 0.2 T_m . $\gamma = 255 \times 10^{-7}\ joul/cm^2$, ΔH_f=2660 $joul/cm^3$.

(b) Calculate the number of atoms in the critical sized nucleus at this undercooling

[Try yourself]

Heterogeneous Nucleation:

Heterogeneous nucleation is a nucleation that occurs in a liquid on the surface of its container, insoluble impurities, and other structural material that lower the critical free energy required to form a stable nucleus. Since large amounts of undercooling do not occur during industrial casting operations and usually range between 0.1 ℃ and 10 ℃, the nucleation must be heterogeneous.

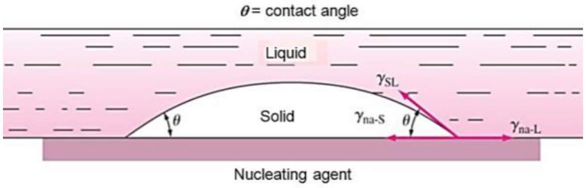


Fig: Heterogeneous nucleation of a solid on a nucleating agent. na= nucleating agent, SL= solid-liquid, S = solid, L= liquid, θ= contact angle

For heterogeneous nucleation to take place, the solid nucleating agent (impurity solid or container) must be wetted by the liquid metal. Also, the liquid should solidify easily on the nucleating agent. Fig. shows a nucleating agent (substrate) that is wetted by the solidifying liquid, creating a low contact angle θ between the solid metal and the nucleating agent. Heterogeneous nucleation takes place on the nucleating agent because the surface energy to form a stable nucleus is lower on this material than in the pure liquid itself (homogeneous nucleation). Since the surface energy is lower for heterogeneous nucleation the total free-energy change for the formation of stable nucleus will be lower and the critical size of the nucleus will be smaller. Thus, a much smaller amount of undercooling is required to form a stable nucleus produced by heterogeneous nucleation.

Cooling Curve

A **cooling curve** is a line graph that represents the change of phase of matter, typically from a gas to a solid or a liquid to a solid. The independent variable (X-axis) is time and the dependent variable (Y-axis) is temperature. The initial point of the graph is the starting temperature of the matter, and generally noted as the "pouring temperature". When the phase change occurs there is a "thermal arrest", that is the temperature stays constant. This is because the matter has more internal energy as a liquid or gas than in the state that it is cooling to. The amount of energy required for a phase change for unit mass of material is known as latent heat. The "cooling rate" is the slope of the cooling curve at any point

Let a liquid is poured into a mold at the pouring temperature, point *A*. The difference between the pouring temperature and the freezing temperature is the superheat. The specific heat is extracted by the mold until the liquid reaches the freezing temperature (point *B*).

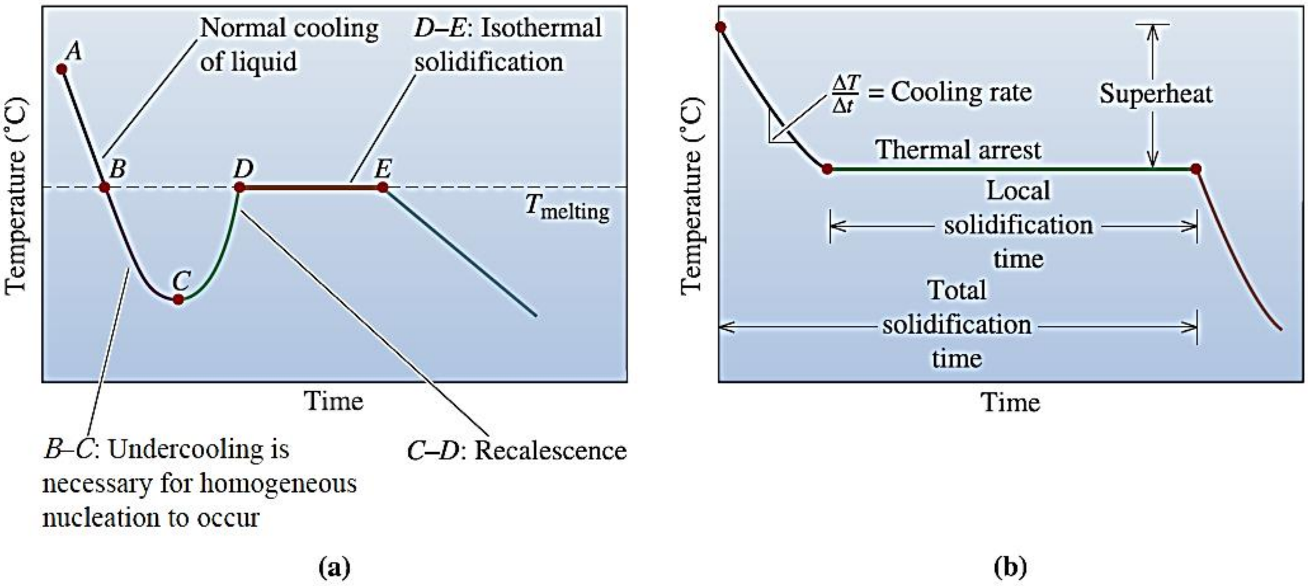


Figure 1: **(a)** Cooling curve for a pure metal that has not been well-inoculated. **(b)** Cooling curve for a well-inoculated, but otherwise pure, metal.

If the liquid is not well-inoculated, it must be undercooled (point *B* to *C*). The slope of the cooling curve before solidification begins is the cooling rate $\frac{\Delta T}{\Delta t}$. As nucleation begins (point *C*), latent heat of fusion is given off, and the temperature rises. This increase in temperature of the undercooled liquid as a result of nucleation is known as **recalescence** (point *C* to *D*). Solidification proceeds isothermally at the melting temperature (point *D* to *E*) as the latent heat given off from continued solidification is balanced by the heat lost by cooling. This region between points *D* and *E*, where the temperature is constant, is known as the **thermal arrest**. A thermal arrest, or plateau, is produced because the evolution of the latent heat of fusion balances the heat being lost because of cooling. At point *E*, solidification is complete, and the solid casting cools from point *E* to room temperature.

If the liquid is well-inoculated, the extent of undercooling and recalescence is usually very small and can be observed in cooling curves only by very careful measurements. If effective heterogeneous nuclei are present in the liquid, solidification begins at the freezing temperature [Figure 1 (b)]. The latent heat keeps the remaining liquid at the freezing temperature until all of the liquid has solidified and no more heat can be evolved. Growth under these conditions is planar. The **total solidification time** of the casting is the time required to remove both the specific heat of the liquid and the latent heat of fusion. Measured from the time of pouring until solidification is complete, this solidification time is approximately given by Chvorinov's rule.

$$t_s = B\left(\frac{V}{A}\right)^2$$

Where, B= Mold constant (sec/m2)
V= volume and A= area of the casting surface

The **local solidification time** is the time required to remove only the latent heat of fusion at a particular location in the casting; it is measured from when solidification begins until solidification is completed. The local solidification times (and the total solidification times) for liquids solidified via undercooled and inoculated liquids will be slightly different.

We often use the terms "melting temperature" and "freezing temperature" while discussing solidification. It would be more accurate to use the term "melting temperature" to describe when a solid turns completely into a liquid. For pure metals and compounds, this happens at a fixed temperature (assuming fixed pressure) and without superheating. "Freezing temperature" or "freezing point" can be defined as the temperature at which solidification of a material is complete.

Problem: Design the thickness of an aluminum alloy casting with a length of 12 in., a width of 8 in. The mold constant in Chvorinov's rule for aluminum alloys cast in a sand mold is 45 min/in^2. Solidification time is 5 minutes.

Solution: From Chvorinov's rule

$$t_s = B\left(\frac{V}{A}\right)^2$$

Where B = 45 min/in^2 and x is the thickness of the casting. Since the length is 12 in. and the width is 8 in.,

$$V = (8)(12)(x) = 96x$$

$$A = (2)(8)(12) + (2)(x)(8) + (2)(x)(12) = 40x + 192$$

$$5 = 45\left(\frac{96x}{40x + 192}\right)^2$$

$$x = 0.77 \text{ in.}$$

Problem: Two castings are produced under identical conditions. One casting has dimension $2cm \times 8cm \times 16cm$ and the other one has $3cm \times 6cm \times 8cm$. Which casting will be stronger?

Solution: We know the solidification time is

$$t_s = B\left(\frac{V}{A}\right)^2$$

So,

$$\frac{(t_s)_1}{(t_s)_2} = \left(\frac{V_1 A_2}{A_1 V_2}\right)^2$$

$$= \left(\frac{(2 \times 8 \times 16) \times \{2(3 \times 6 + 6 \times 8 + 8 \times 3)\}}{\{2(2 \times 8 + 8 \times 16 + 16 \times 2)\} \times (3 \times 6 \times 8)}\right)^2$$

$$= 0.826$$

$$(t_s)_1 = 0.826(t_s)_2$$

We know, that the smaller solidification time will produce more grains and stronger casting. So that $2cm \times 8cm \times 16cm$ casting will be stronger.

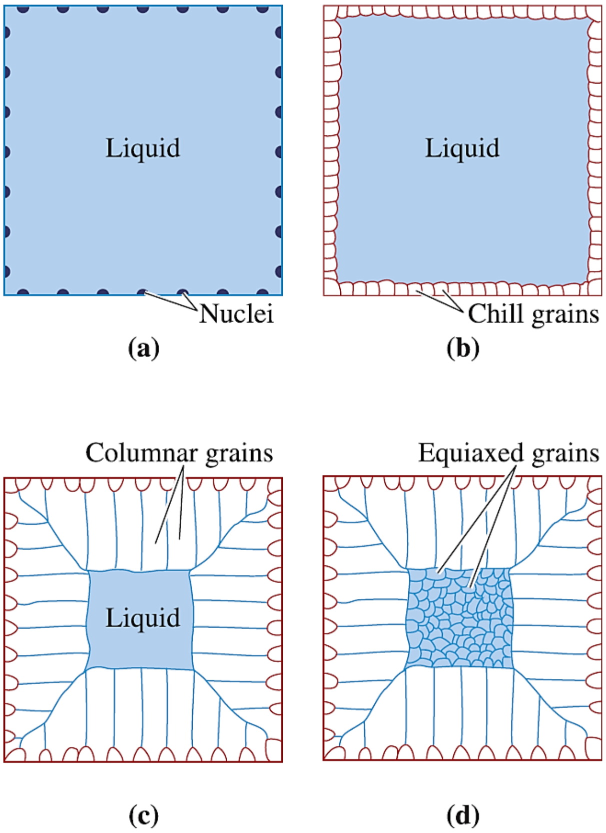
Cast Structure

In manufacturing components by casting, molten metals are often poured into molds and permitted to solidify. The mold produces a finished shape, known as a ***casting***. In other cases, the mold produces a simple shape called an **ingot**. An ingot usually requires extensive plastic deformation before a finished product is created.

A ***macrostructure*** sometimes referred to as the **ingot structure**, consists of as many as three regions

i) Chill Zone The **chill zone** is a narrow band of randomly oriented grains at the surface of the casting. The metal at the mold wall is the first to cool to the freezing temperature. The mold wall also provides many surfaces at which heterogeneous nucleation takes place.

ii) **Columnar Zone** The **columnar zone** contains elongated grains oriented in a particular crystallographic direction. As heat is removed from the casting by the mold material, the grains in the chill zone grow in the direction opposite to that of the heat flow, or from the coldest toward the hottest areas of the casting. This tendency usually means that the grains grow perpendicular to the mold wall. Grains grow fastest in certain crystallographic directions. In metals with a cubic crystal structure, grains in the chill zone that have a $< 100 >$ direction perpendicular to the mold wall grow faster than other less favorably oriented grains . Eventually, the grains in the columnar zone have $< 100 >$ directions that are parallel to one another, giving the columnar zone anisotropic properties. This formation of the columnar zone is influenced primarily by growth—rather than nucleation—phenomena. The grains may be composed of many dendrites if the liquid is originally undercooled. The solidification may proceed by planar growth of the columnar grains if no undercooling occurs.

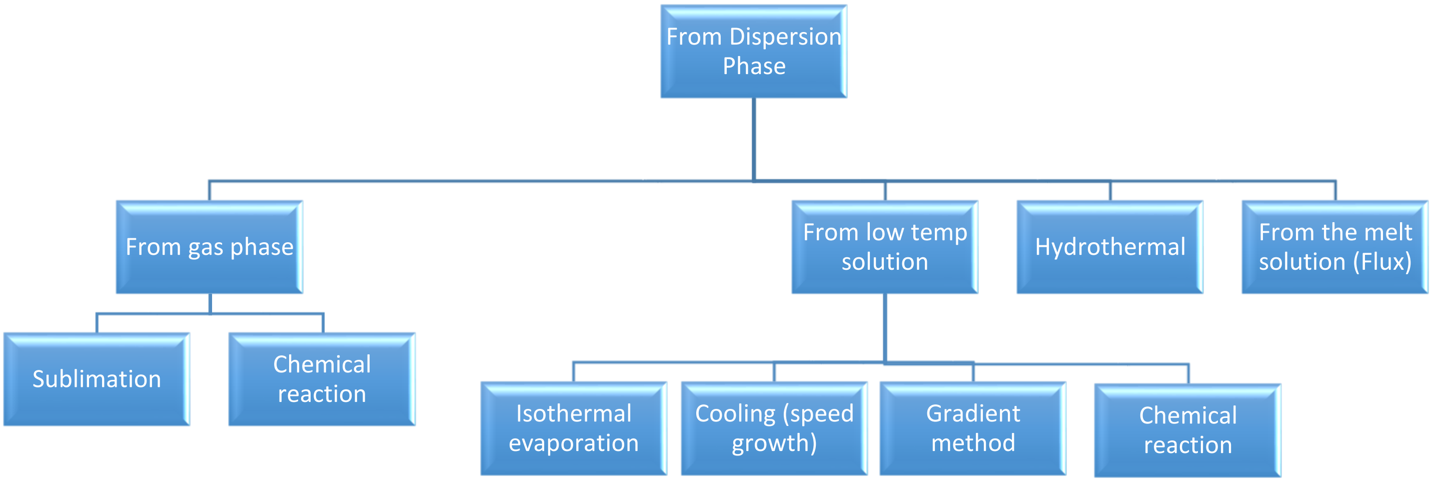


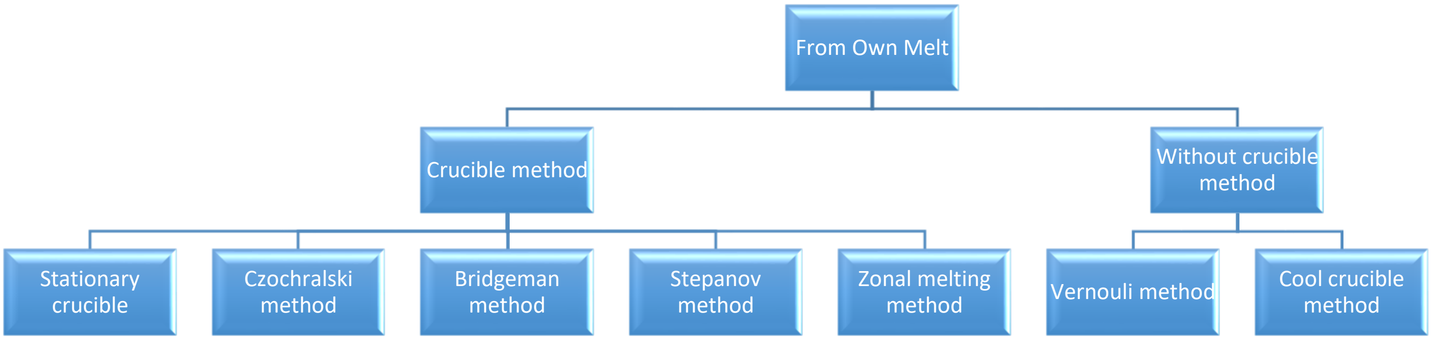
(a) (b) (c) (d)

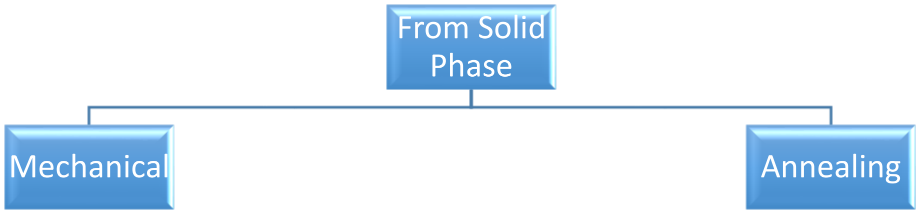
Figure 1: Development of the ingot structure of a casting during solidification: (a) nucleation begins, (b) the chill zone forms, (c) preferred growth produces the columnar zone, and (d) additional nucleation creates the equiaxed zone.

iii) Equiaxed Zone *(having approximately equal dimensions in all directions)*

Although the solid may continue to grow in a columnar manner until all of the liquid has solidified, an equiaxed zone frequently forms in the center of the casting or ingot. The **equiaxed zone** contains new, randomly oriented grains, often caused by a low pouring temperature, alloying elements, or grain refining or inoculating agents. Small grains or dendrites in the chill zone may also be torn off by strong convection currents that are set up as the casting begins to freeze. These also provide heterogeneous nucleation sites for what ultimately become equiaxed grains. These grains grow as relatively round, or equiaxed, grains with a random orientation, and they stop the growth of the columnar grains. The formation of the equiaxed zone is a nucleation-controlled process and causes that portion of the casting to display isotropic behavior. By understanding the factors that influence solidification in different regions, it is possible to produce castings that first form a "skin" of a chill zone and then dendrites. Metals and alloys that show this macrostructure are known as **skin-forming alloys**. We also can control the solidification such that no skin or advancing dendritic arrays of grains are seen; columnar to equiaxed switchover is almost at the mold walls. The result is a casting with a macrostructure consisting predominantly of equiaxed grains. Metals and alloys that solidify in this fashion are known as **mushy-forming alloys** since the cast material seems like a mush of solid grains floating in a liquid melt. Many aluminum and magnesium alloys show this type of solidification.


From Dispersion Phase
From gas phase
From low temp solution
Hydrothermal
From the melt solution (Flux)
Sublimation
Chemical reaction
Isothermal evaporation
Cooling (speed growth)
Gradient method
Chemical reaction

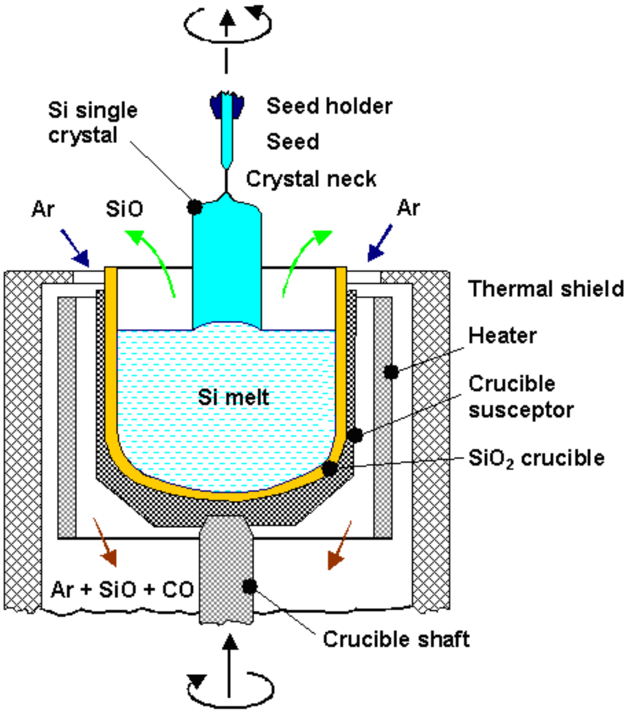

From Own Melt
Crucible method
Without crucible method
Stationary crucible
Czochralski method
Bridgeman method
Stepanov method
Zonal melting method
Vernouli method
Cool crucible method


From Solid Phase
Mechanical
Annealing

Crystal Growth Methods:

Czochralski Method

The techniques that have been developed to grow large single crystals of the commercially important semiconductors are generally applicable to other elements and compounds. The rate of growth of a crystal from its own liquid is determined primarily by the rate of out flow of heat of fusion from the growing crystal face; it is necessary to maintain this out-flow rate, so that temperature remains below the melting points. A widely used procedure for growing large crystals form the melt called Czochralski method, start the growth by immersing a previously oriented seed crystal into the surface of the melt and slowly withdrawing it as growth proceeds. Czochralski method is the standard procedure which is used for growing silicon and germanium single crystal. A linear growth rate as high as $(3 \times 10^{-4}\ m/s)$ are possible in this method.



The temperature of the crystal melt interface is controlled by the rate of pulling by controlling the temperature gradient in the crystal and by controlling the temperature of the melt. At first the melt is kept slightly above the melting point and the seed is lowered into the liquid. The tip of the seed is first melted to make sure that the liquid wets its surface and then the temperature is reduced until the melt begins to freeze onto the seed. The seed is then slowly raised in order to maintain the liquid-solid interface near the surface of the melt. It is a common practice to rotate the seed during growth to promote stirring in the melt and smear out any slight temperature asymmetries. If necessary, the whole apparatus is placed inside the high vacuum or in inert atmosphere to reduce oxidation and contamination.

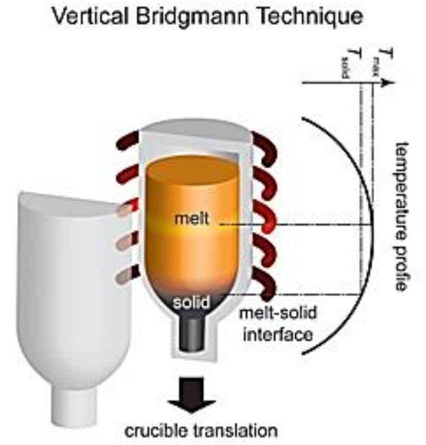
In growing single crystal, solidification must take place around a single nucleus, so that no other crystal are nucleated and grown. To accomplish this, the interface temperature between solid and liquid must be slightly lower than the melting point of the solid and liquid temperature must increase beyond the interface. To achieve this temp gradient, the latent heat (Gibb's free energy) of solidification must be conducted through solidifying solid crystal. The growth rate of this crystal must be slow that the temp at the liquid-solid interface slightly below the melting point of the solidifying solid. Part of the surface of the seed crystal is melted in the liquid to remove the outer strain region and to produce a surface for the liquid to solidify one. The seed crystal continues to rotate and is slowly raised on the melt. As it is raised from the melt, crystal from the liquid in the crucible adheres to crucible and grows on the seed crystal, produce a larger diameter single crystal.

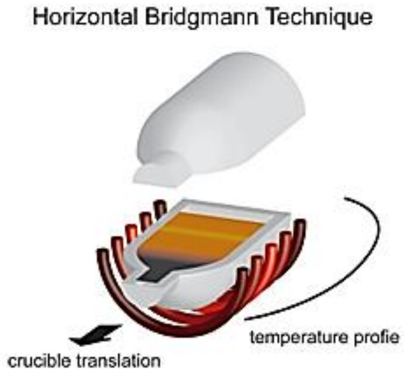
Bridgman method:

The Bridgman technique (also known as Bridgman-Stockbarger method) is one of the oldest techniques used for growing crystals. Similar to Czochralski technique, the Bridgman technique employs also a crystal growth from melt.

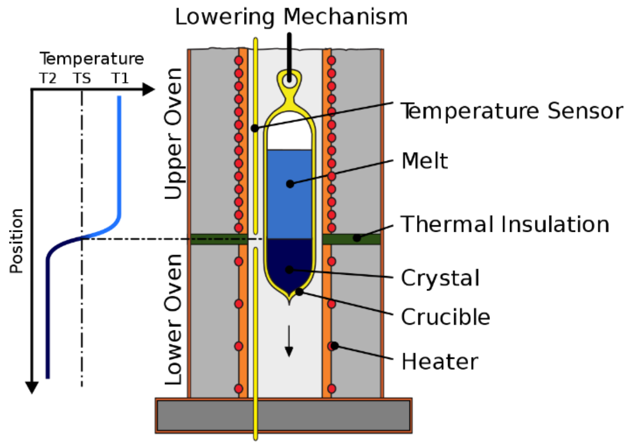
In Bridgman technique the crucible containing the molten material is translated along the axis of a temperature gradient in a furnace, whereas in Stockbarger technique, which is just a modification to the Bridgman technique, there is a high-temperature zone, an adiabatic loss zone and a low-temperature zone. These two methods are very often not specifically differed in the terminology.

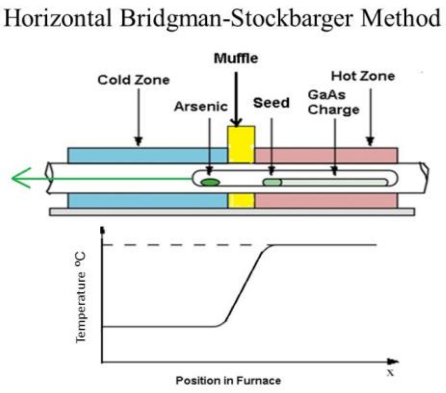
The principle of the Bridgman technique is the directional solidification by translating a melt from the hot zone to the cold zone of the furnace. At first the polycrystalline material in the crucible needs to be melted completely in the hot zone and be brought into contact with a seed at the bottom of the crucible. This seed is a piece of single crystal and ensures a single-crystal growth along a certain crystallographic orientation. Part of the seed will be re-melted after the contact with the melt. This provides a fresh interface for the crystal growth.





The crucible is then translated slowly into the cooler section of the furnace. The temperature at the bottom of the crucible falls below the solidification temperature and the crystal growth is initiated by the seed at the melt-seed interface. After the whole crucible is translated through the cold zone the entire melt converts to a solid single-crystalline ingot.

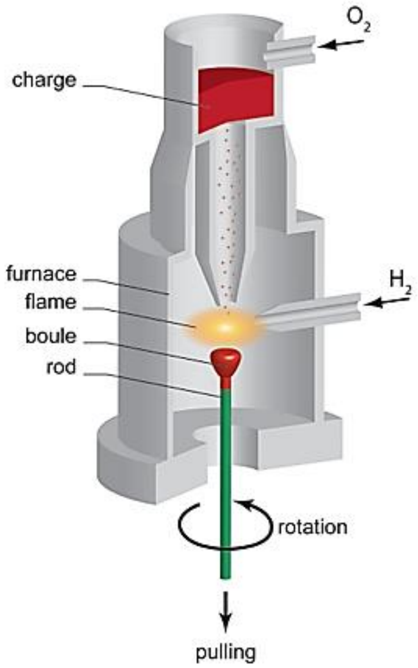




The Bridgman technique can be implemented in either a vertical (vertical Bridgman technique) or a horizontal system configuration (horizontal Bridgman technique). The concept of these two configurations is similar. The vertical Bridgman technique enables the growth of crystals in circular shape, unlike the D-shaped ingots grown by horizontal Bridgman technique. However, the crystals grown horizontally exhibit high crystalline quality (e.g., low dislocation density) since the crystal experiences lower stress due to the free surface on the top of the melt and is free to expand during the entire growth process.

Instead of moving the crucible, the furnace can be translated from the seed end while the crucible is kept stationary. In this manner a directional solidification can be achieved, too. A further modification is the so called gradient freezing technique, with which neither the crucible nor the furnace needs to be translated. Instead, a translation of the temperature gradient is implemented by using a multiple-zone furnace wherein the power to each zone is programmed and controlled by individual controllers. This system can maintain the same temperature gradient at the liquid-solid (i.e. melt-crystal) interface, which changes in turn its location with time during the growth. Analogous to the Bridgman technique, the gradient freezing technique can also be realized in vertical and horizontal configurations.

Verneuil Method

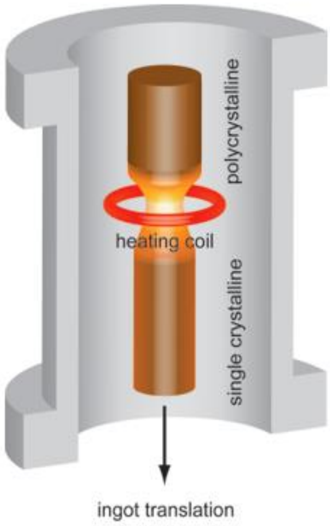


Verneuil method (also called flame fusion technique) was one of the earliest melt techniques used to grow large quantity of crystals with high melting temperature. It was first introduced by the French chemist Auguste Verneuil and originally developed for producing synthetic gemstones. Today the technique is still used to grow a variety of high-quality crystals such as corundum (Al_2O_3), spinel ($MgAl_2O_4$), rutile (TiO_2) and strontium titanate ($SrTiO_3$), which are widely applied in laser devices and precision instruments, as well as in thin film technologies as substrates.

The Verneuil process involves essentially a furnace with oxygen and hydrogen supply, highly fine powder source as starting material and a support rod either with or without a seed crystal depending on the desired crystallographic orientation of the crystal to be grown.

During the crystal growth, the source material is continuously released into the furnace chamber through a narrow tube and mixed with compressed oxygen. At the outlet of the tube the powder is fed into an oxygen/hydrogen flame of about 2200 °C. As the powder passes through this flame, it melts into fine droplets which fall onto the support rod. A sinter cone is gradually formed by the droplets and serves as a seed for crystal growth. As more droplets are fed to the seed the support rod is lowered slowly from the flame, allowing a cylindrical single crystal, a boule, to form. The term boule originates from the French word for swelling and refers to the ball-like appearance of the first resulted crystal. Typical produced boules grow up to about 100 mm in length and 15 to 20 mm in diameter, although the cross-section of the boule is not always circular. After growth the boule is parted lengthwise to relieve internal stress and avoid fracture.

Floating zone technique



Zone refining, a precursor of floating zone technique, was first developed by W. G. Pfann in 1951 at Bell Laboratories and later modified by different people independently. Originally the floating zone technique was used for manufacturing silicon crystal, but today it can also be applied for growing single crystals of various congruently and incongruently melting oxides.

During the floating zone process, a polycrystalline crystal is translated slowly through a heater and a narrow region on the crystal will be molten (floating zone). At the liquid-solid interface, the impurities diffuse from solid region into liquid region and segregate at the end of the ingot after the whole crystal passes through the heater. In order to grow a single crystal, a seed crystal having a certain orientation needs to be brought into contact with the molten region at the beginning of the process.

A variety of heating systems can be used for floating zone technique, including induction coil, resistance heater or more recently optical heating system containing high-power halogen lamps and ellipsoidal mirrors.

The main advantages of the floating zone technique are that no crucible is necessary, which results in a high purity of the grown crystal, and both congruently and incongruently melting materials can be grown by this method.

Calcination:

Calcination is a thermal treatment process in the absence or limited supply of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition. A calciner is a steel cylinder that rotates inside a heated furnace and performs indirect high-temperature processing (550–1150 °C, or 1000–2100 °F) within a controlled atmosphere.

Examples of calcination processes include the following:

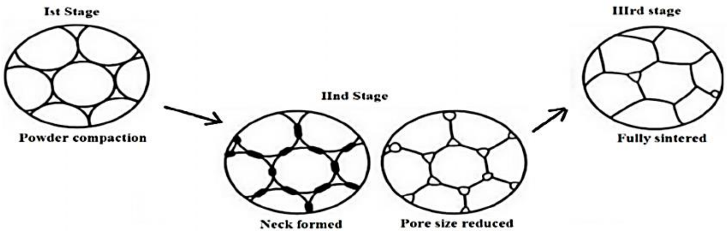
- decomposition of carbonate ores, as in the calcination of limestone to drive off carbon dioxide; $CaCO_3 \overset{\Delta}{\rightarrow} CaO + CO_2$
- decomposition of hydrated minerals, as in the calcination of bauxite ($Al(OH)_3$) and gypsum ($CaSO. 2H_2O$), to remove water of crystallization as water vapor;
- decomposition of volatile matter contained in raw petroleum coke;
- heat treatment to effect phase transformations, as in conversion of anatase to rutile polymorph or devitrification (*growth of crystalline structures within or on the surface of glass*) of glass materials
- removal of ammonium ions in the synthesis of zeolites.

Sintering:

Sintering or **frittage** is the process of compacting and forming a solid mass of material by heat or pressure without melting it to the point of liquefaction. Sintering happens naturally in mineral deposits or as a manufacturing process used with metals, ceramics, plastics, and other materials. The atoms in the materials diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece.

Because the sintering temperature does not have to reach the melting point of the material, sintering is often chosen as the shaping process for materials with extremely high melting points such as tungsten (3,422 °C) and molybdenum (2,623 °C). The study of sintering in metallurgy powder-related processes is known as *powder metallurgy*.

An example of sintering can be observed when ice cubes in a glass of water adhere to each other, which is driven by the temperature difference between the water and the ice. Examples of pressure-driven sintering are the compacting of snowfall to a glacier, or the forming of a hard snowball by pressing loose snow together.



Glass:

A glass is a ceramic material in that it is made horn inorganic materials at high temperatures. However, it is distinguished from other ceramics in that its constituents are heated to fusion and then cooled to a rigid state without crystallization. Thus, a glass can he defined as an inorganic product of fusion that has cooled to a rigid condition without crystallization. A characteristic of a glass is that it has a non-crystalline or amorphous structure. The molecules in a glass are not arranged in a regular repetitive long-range order as exists in a crystalline solid. In a glass, the molecules change their orientation in a random manner throughout the solid material.

Glass Transition Temperature

The solidification behavior of a glass is different from that of a crystalline solid, as illustrated in Fig. 1, which is a plot of specific volume (reciprocal of density) versus temperature for these two types of materials. A liquid that forms a crystalline solid upon solidifying (i.e., a pure metal) will normally crystallize at its melting point with a significant decrease in specific volume, as indicated by path ABC in Fig. 1. In contrast, a liquid that forms a glass upon cooling does not crystallize but follows a path like AD in Fig. 1. Liquid of this type becomes more viscous as its temperature is lowered and transforms from a rubbery, soft plastic state to a rigid, brittle glassy state in a narrow temperature range where the slope of the specific volume versus temperature curve is markedly decreased. The point of intersection of the two slopes of this curve define a transformation point called the glass transition temperature Tg. This point is structure-sensitive, with faster cooling rates producing higher values of Tg.

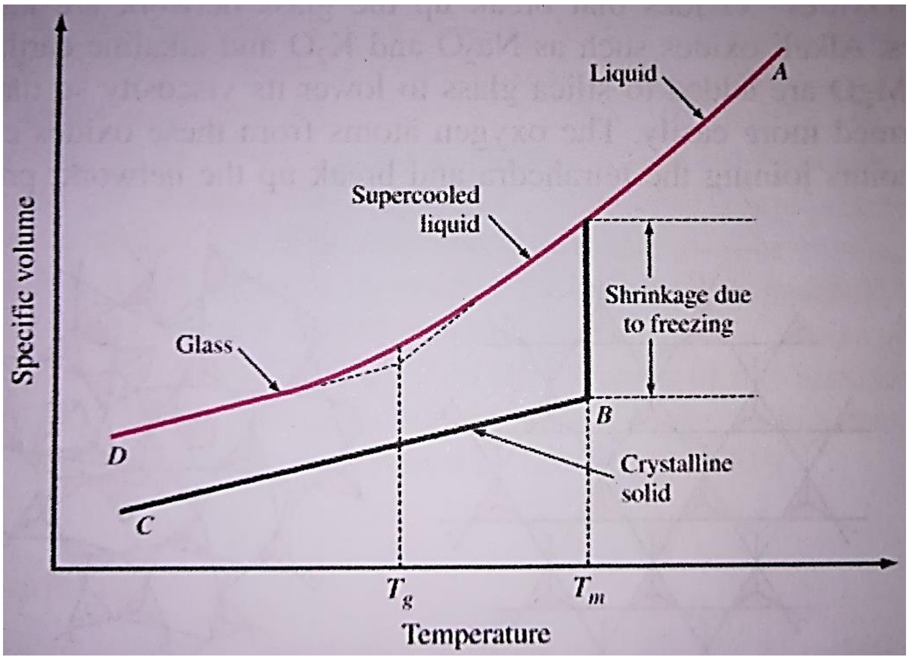


Figure 1: Solidification of crystalline and glassy (amorphous) materials showing changes in specific volume. Tg is the glass transition temperature of the glassy material. Tm, is the melting temperature of the crystalline material.

Non-equilibrium and thermodynamic Views of Glass Transition

We know that, a prerequisite of glass formation is the prevention of nucleation and crystal growth during cooling of the glass melt. Once the temperature has been reduced at a faster rate, it is more likely that the melt will solidify into glassy form. Accordingly, there is a temperature dependence of nucleation rate ant crystal growth rate ant both of these rates pass through a maximum as diagrammatically shown in fig.1.

This figure shows that, glass formation has some relation with the dynamics of flow or we can say with the viscous flow. So it may be a non-equilibrium transformation. In equilibrium transition there occurs a structural or configurational change in the system at some well-defined temperature (e.g. T_m). But in relaxation mechanism, there is ever-changeable system variables and the system always undergoes through a slowly changing environment produced by external forces and reestablishment of equilibrium is not possible after a change has taken place. In stabilization experiments at temperature T we see that the equilibrium can be attained from both sides of volume V (or H, S) as shown in Fig. 2

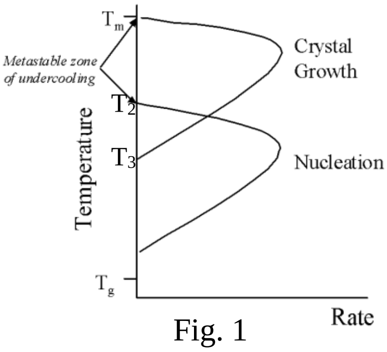


Fig. 1

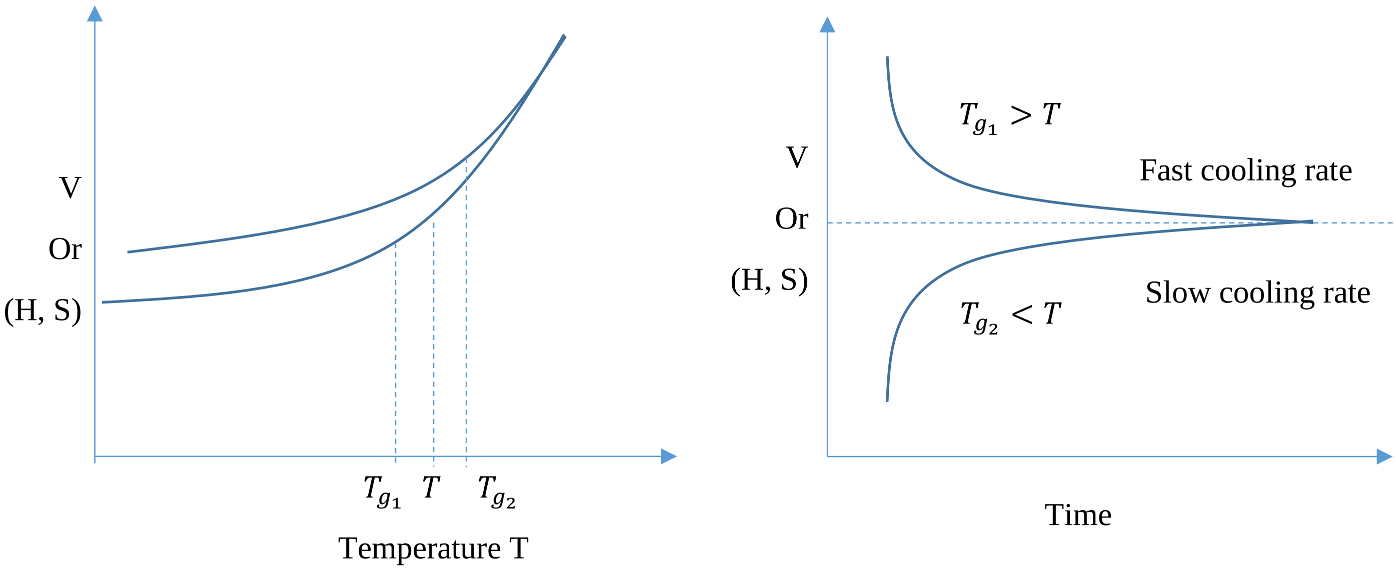


Fig. 2

The nucleation rate (I) depends on the inverse of viscosity (kinetic barrier) and the magnitude of the thermodynamic driving force. The thermodynamic driving force is a balance between the volume free energy of the stable nuclei (proportional to r^3*, where r is the nucleus radius) and the surface energy associated with the creation of new solid-liquid interfaces (proportional to* r^2*). The critical nucleus radius is that where an increase in size means a decrease in energy, where the volume energy gained during nucleus formation overcomes the surface energy expended.*

The nucleation rate curve is at a lower temperature than the crystal rate curve because of this surface energy barrier. Undercooling the melt below the melting point (T_m), increases the thermodynamic contribution to the rate equation, increasing nucleation rate. At the same time, viscosity is increasing, slowing down material transport. When cooled to low enough temperature, approaching the glass transition temperature (Tg) the nucleation and crystal growth rates go to zero.

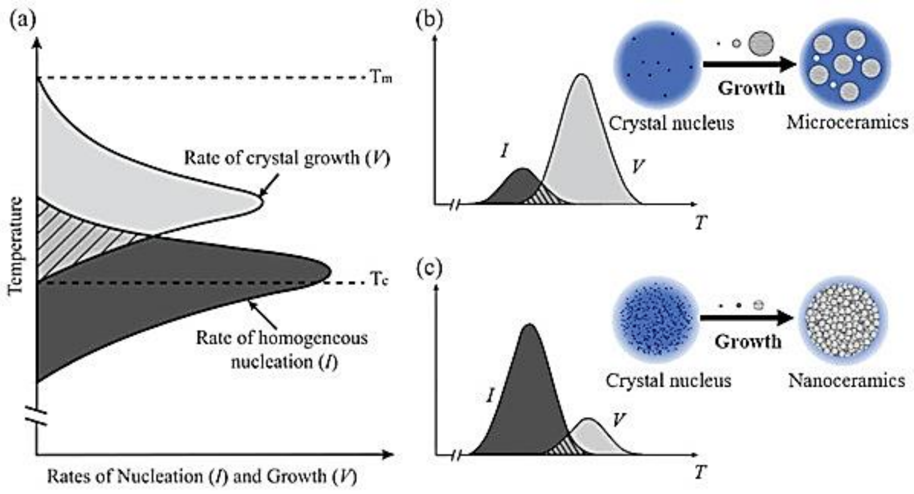
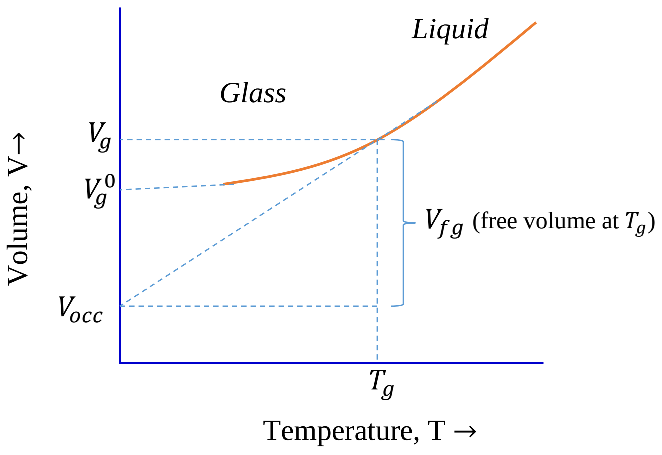


Fig. 3

Glass Transition Model (Gee’s Model or Thermodynamic Model):

The total volume of the glass forming liquid is divided into two parts;

1) A part occupied by the molecules (atoms)
2) Another part in which the molecules are free to move.



A glass is distinguished from the liquid in two ways:

i) In the glassy phase the free volume remains constant, i.e., independent of temperature (hard fixed volume)
ii) The redistribution of holes no longer occurs. The positions of molecules are fixed (frozen in volumes)

But in liquid state, both of these volumes are variable. The glass liquid relationship can then be as follows-

Let α_{liq} be the expansion coefficient of liquid glass and α_g be the expansion coefficient of solid glass. Then the expansion coefficient of the free volume is

$$\Delta\alpha = \alpha_{liq} - \alpha_g \qquad (1)$$

If the total volume of glass is V_g at temperature T_g, then the free volume V_f at any temperature $T > T_g$ will be

$$V_f = V_{fg} + V_g \Delta\alpha (T - T_g) \qquad (2)$$

Where, V_{fg} is the free volume of the glass at transition.

The same argument can be applied to the effect of pressure. If k is the compressibility then,

Compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure change. $k = \frac{1}{V}\frac{\partial V}{\partial P}$

$$\Delta k = k_{liq} - k_g \qquad (3)$$

The combined effect of temperature and pressure P on the free volume is

$$V_f = V_{fg} + \underbrace{V_g \Delta\alpha \left(T^P - {T_g}^0\right)}_{\text{Due to temp.}} - \underbrace{V_g \Delta k P}_{\text{Due to pressure}} \qquad (4)$$

Where, ${T_g}^0$ and T^P represent T_g at zero pressure and T at P pressure respectively.

In this expression (4), somehow if $V_f = V_{fg}$ is true at $T = T_g$, we get,

$$V_{fg} = V_{fg} + V_g \Delta\alpha \left(T^P - {T_g}^0\right) - V_g \Delta k P$$

$$V_g \Delta\alpha \left(T^P - {T_g}^0\right) = V_g \Delta k P$$

$$\frac{T^P - {T_g}^0}{P} = \frac{\Delta k}{\Delta\alpha}$$

$$\therefore \frac{T^P - T_g{}^0}{P - 0} = \frac{\partial T}{\partial P} = \frac{\Delta k}{\Delta \alpha} \qquad at\ pressure\ P$$

Several arguments have been put forward to estimate V_f. For example, with some approximation if we consider that $T=0K$, there is no free volume. Then the extrapolated value of V_g at T=0k is V_{occ} (Occupied) i.e.,

$$V_{liq} = V_g\{1 + \alpha_{liq}(T - T_g)\}$$

$$V_{occ} = V_g(1 - \alpha_{liq}T_g) \qquad \boxed{V_{liq} = V_{occ} \quad at \quad T=0K} \qquad (5)$$

On the other hand, total volume, V_g at T=0k can be written as

$$V_g{}^0 = V_g(1 - \alpha_g T_g) \qquad (6)$$

Then from the volume-temperature diagram, we see that,

$$V_{fg} = V_g{}^0 - V_{occ}$$

$$= V_g(1 - \alpha_g T_g) - V_g(1 - \alpha_{liq}T_g)$$

$$= T_g V_g(\alpha_{liq} - \alpha_g) = T_g V_g \Delta\alpha$$

So

$$T_g \Delta\alpha = \frac{V_{fg}}{V_g} \qquad (7)$$

For polymeric glasses where $T_g\Delta\alpha$ was found to vary approximately between 0.08 to 0.13 at T_g. i.e., about 11% of the total volume is the free volume of the glass.