- Primary nucleation is the formation of a solid phase from a clear liquid. Primary nucleation is usually categorized as homogeneous nucleation and heterogeneous nucleation.
  - Homogeneous nucleation occurs in the pure bulk solution. It is determined by the formation of stable nuclei in a supersaturated solution, which means molecules of solute come close together to form the nuclei.[7]
  - Heterogeneous nucleation is induced by foreign surfaces such as impurities present in the solution and can become significant at much lower supersaturation levels than homogeneous primary nucleation.

The first and most famous theory to describe nucleation processes is the classical nucleation theory (CNT). CNT is based on the condensation of a vapor from a liquid, but it may be extended to crystallization from melts and solutions. The theory considers that the overall excess free energy (ΔG) between the small spherical particle (with r radius) and the solution is given by the sum of the surface excess free energy (ΔG_s) and the volume excess free energy (ΔG_v). The former is often called "surface term", and the latter "volume term". The surface term is the excess free energy between the surface of a particle and the bulk of a particle and it is a positive quantity, which is proportional to the particle surface. The volume term is the excess free energy between a very large particle ($r \to \infty$) and the bulk solution, which is a negative quantity proportional to the particle volume. The overall free energy of a particle with radius r then can be written as:

$$\Delta G = \Delta G_v + \Delta G_s = 4\pi r^2 \sigma_s + \frac{4}{3}\pi r^3 \Delta G_v \tag{2.1}$$

where σ_s (N m^{-1}) is the interfacial tension and ΔG_v (J m^{-3}) is the free energy change of transformation per unit volume. Taking the derivative of ΔG with respect to the radius, eqn (2.1) becomes:

$$\frac{d(\Delta G)}{dr} = 8\pi r \sigma_s + 4\pi r^2 \Delta G_v \tag{2.2}$$

Taking into account that the second term of eqn (2.2) is a negative quantity, it is obvious that eqn (2.2) has a maximum. This maximum is the critical radius (r_c) of the *nuclei*: below this size, the free energy of the cluster decreases if the radius decreases (*i.e.* the cluster dissolves), and over this radius the free energy decreases with the radius, so the cluster reduces its free energy by growth. Therefore, r_c is considered to be the smallest stable *nuclei* size under the given set of thermodynamic conditions.

$$r_c = -\frac{2\sigma_s}{\Delta G_v} \tag{2.3}$$

The critical activation energy, *i.e.* the activation energy belonging to r_c, can be expressed from eqn (2.1) and (2.3) (Figure 2.3):