Thus, while an unseeded batch cooling crystallization process usually relies on primary nucleation to provide the crystals, during a continuous crystallization process the omnipresent crystals continuously generate more crystals through secondary nucleation. Only in extreme cases are there indications that homogeneous nucleation is the dominant nucleation mechanism. Introduction of crystals into a crystallization process is based on either nucleation or seeding. Seeding relies on addition of previously formed crystals while nucleation implies birth of new crystals. The nucleation rate expresses the number of new crystals that are generated per unit of time per unit solution volume at a given composition and temperature. Nucleation events could be evenly distributed across the bulk fluid volume. However, it may more often be the case that locally extreme conditions (supersaturation, fluid dynamics, mixing points) lead to local nucleation events. While the resulting suspension is distributed over the entire crystallizer, the generation of crystals through nucleation can be highly localized.

1.2.1 Primary Nucleation

In supersaturated solutions, the nucleation rate varies highly non-linearly with supersaturation. Classical Nucleation Theory describes the supersaturation dependent nucleation rate J as a function of a supersaturation dependent nucleation barrier $B/\ln^2 S$:[9,10]

$$J = AS\exp(-B/\ln^2 S) \tag{1.2}$$

where A and B are constants. The nucleation barrier is very large for supersaturated solutions close to the solubility line resulting in a negligible nucleation rate and prolonged lifetimes of the metastable solutions. At very high supersaturations, far away from the solubility line, the energy barrier for nucleation vanishes and spinodal decomposition takes over from nucleation.

The values of the nucleation rate constants A and B depend on the primary nucleation rate mechanism taking place.[6] Primary nucleation can take place in the bulk volume of a particle free solution (homogeneous primary nucleation) or at interfaces (heterogeneous primary nucleation) due to the presence of crystallizer wall, solution–air interface and suspended foreign particles such as dust particles. Heterogeneous particles or surfaces promoting heterogeneous nucleation are characterized by B-values that are much lower than those in the case of homogeneous nucleation from a clear solution: the enhanced heterogeneous nucleation is due to the reduction of the nucleation barrier. This, even though the A-value for heterogeneous nucleation is orders of magnitude lower than that for homogeneous nucleation. Since there will always be interfaces or particles present in industrial solutions to nucleate onto, often heterogeneous nucleation is assumed to be the dominant primary nucleation mechanism.