

heat transfer to the crystals and the surroundings can affect the crystal nucleation, growth and dissolution processes. This is because the driving force of the crystallization is supersaturation which is a function of concentration and temperature.

This section is aimed to provide a brief insight into the modeling of fundamental crystallization mechanisms, namely, the nucleation, growth, agglomeration and breakage of crystals. As usually all crystallization sub-processes are lumped into the same PBE, the adequate description of individual mechanisms is paramount.

### 2.2.1 The Supersaturation

The concepts of solubility and supersaturation are vital in developing and characterizing the behavior of crystallization systems. The solubility, also called saturation concentration ( $c_s$ ), is defined as the amount of a substance (solute) that can be dissolved in a given amount of solvent at given set of thermodynamic conditions (temperature, pressure *etc.*). Under certain conditions the actual solute concentration ( $c$ ) might exceed the solubility, in which case the solution is said to be supersaturated. Supersaturated solution is metastable, and given enough time, the solution will come back to its saturation concentration by crystallizing additional solute. If the actual concentration is lower than the solubility, the solution is undersaturated. Table 2.1 summarizes the widely used expressions for the supersaturation.

There are four methods that are broadly used to generate supersaturation:<sup>6</sup>

- *Cooling.* The solubility often increases with the temperature, therefore, supersaturation can be generated by cooling a high temperature, highly concentrated solution.
- *Evaporation.* The solute concentration can be increased by removing the solvent from the system *via* evaporation. Therefore, the solute can be concentrated by evaporation until reaching and passing the solubility.
- *Antisolvent addition.* The solubility depends on solvent nature; the solubility can significantly differ in different solvents. In this case, the solvent in which the solubility is higher is called “solvent”, whereas the low solubility solvent is called “antisolvent”. Preparing a highly concentrated solution in the “solvent” and then adding antisolvent to it leads to solubility decrease, hence, generates supersaturation.

**Table 2.1** Widely used supersaturation expressions.

Mechanism	Model-equation	Remark
Supersaturation ratio	$S = \frac{c}{c_s}$	dimensionless. $S = 1$ indicates saturated solution
Absolute supersaturation	$\Delta c = c_s - c$	expressed in units of concentration
Relative supersaturation	$\sigma = \frac{c - c_s}{c_s} = S - 1$	dimensionless. $\sigma = 0$ indicates saturated solution