

Table 2.2 Summary of commonly used empirical and semi-empirical nucleation rate models.

Mechanism	Model-equation	Remark
Homogeneous nucleation	$B = k_b \exp \left[\frac{-16\pi\sigma_s^3 v^2}{3k^3 T^3 \ln^2(S)} \right]$	σ_s : interfacial tension; v : molecular volume; k : Boltzmann constant
Heterogeneous nucleation	$B = k_b \exp \left[\frac{-16\pi\sigma_s^3 v^2 f(\varphi)}{3k^3 T^3 \ln^2(S)} \right]$	Extra factor $f(\varphi)$ is to consider foreign surface effects
Two step nucleation	$B = \frac{k_2 C_1 T \exp \left(-\frac{\Delta G_2^*}{k_B T} \right)}{\eta(C_1, T) \left[1 + \frac{U_1}{U_0} \exp \left(\frac{\Delta G_C^0}{k_B T} \right) \right]}$	Two step nucleation rate model. See the literature for details ⁸
Primary nucleation ^a	$B = k_b \sigma^b$	Commonly used nucleation expression
Secondary nucleation ^a	$B = k_b \sigma^b \mu_2$	μ_2 : second moment (see eqn (2.46))
	$B = k_b \sigma^b \mu_3$	μ_3 : third moment (see eqn (2.46))
	$B = k_b \sigma^b \mu_3^j \exp \left(-\frac{E_b}{RT} \right)$	E_b : activation energy; R : gas constant
	$B = k_b \sigma^b \mu_3^j N^k$	N : impeller stirring rate

^aBoth relative and absolute supersaturation can be used.

2.2.3 Growth and Dissolution

The newly born *nuclei* and existing crystals in the supersaturated solution grow with time. From the mass transfer point of view, three major successive steps are required for the crystal growth process to happen, which are illustrated in Figure 2.4:

- convective mass transport of solute molecules from the bulk solution to the boundary layer of the crystal, which in a well-mixed system is usually significantly faster than the
- conductive (diffusive) mass transport through the boundary layer to the crystal surface and
- surface integration of the molecule to the crystal lattice.

The diffusion step can be described by the diffusion equation, which, in terms of notations of Figure 2.4 has the form:

$$\dot{m}_{c,d} = \frac{dm_{c,d}}{dt} = DA \frac{c - c_i}{\delta} = k_d A (c - c_i) \quad (2.5)$$

where D ($m^2 s^{-1}$) is the diffusion coefficient and A (m^2) is the crystal surface. The surface integration step is characterized by: