with

$$k_5 = \frac{DV_{\mathrm{m}}}{d} \tag{17.38}$$

where k_5 is a constant that determines the maximum growth rate for a given system and d is the molecular diameter. This mechanism of crystal growth gives rise to rounded crystal surfaces.

Nucleation of two-dimensional clusters mechanism: In cases where the crystal face is smooth, growth can occur by either a two-dimensional nucleation mechanism or by a spiral-growth mechanism. For two-dimensional nucleation, growth occurs by attachment of molecules to the edge of a nucleus on the surface. Under ideal conditions, the growing step on a crystal surface will advance across the crystal face until that particular layer is complete. Before another layer starts, a center of crystallization has to form via surface nucleation. The growth rate for this mechanism is exponentially dependent on the driving force:

$$G = k_6 c_{\mathrm{t}}^{1/3}\left[\ln\left(\frac{c_{\mathrm{t}}}{c_{\mathrm{s}}}\right)\right]^{5/6} \exp\left[-\left(\frac{\pi\gamma^2}{3\left(k_{\mathrm{B}}T\right)^2}\right)\ln\left(\frac{c_{\mathrm{t}}}{c_{\mathrm{s}}}\right)\right] \tag{17.39}$$

with

$$k_6 = \left(\frac{2\pi}{3}\right)^{1/3}\left[\frac{2D_{\mathrm{S}}n_{\mathrm{S}}V_{\mathrm{m}}}{\lambda\alpha}\right] \tag{17.40}$$

where k_{B} is Boltzmann's constant, D_{S} is the surface diffusion coefficient, n_{S} is the surface solute density, λ is the mean diffusion distance, and α is the lattice spacing.

Spiral-growth mechanism: Another model to describe crystal growth in the presence of smooth crystal faces is the spiral-growth mechanism. The presence of screw-lattice dislocations acts as a continuous source of steps. Surface nucleation is therefore not necessary, and the crystal can grow as if covered with kinks. Under these conditions, there is never a flat face, and growth proceeds at the maximum theoretical rate for the particular level of supersaturation. This model was developed by Burton et al. (1951). It describes the situation where crystal growth occurs via addition of growth units to kink sites for a series of equidistant steps. The curvature of the ensuing spiral is related to the spacings of the successive turns and to the degree of supersaturation. The growth rate is given as follows:

$$G = k_7 c_{\mathrm{t}}\left[\ln\left(\frac{c_{\mathrm{t}}}{c_{\mathrm{s}}}\right)\right]^2 \tag{17.41}$$

with

$$k_7 = \frac{0.05Dk_{\mathrm{B}}T}{\gamma} \tag{17.42}$$

At low supersaturation, Equation 17.41 predicts that the rate of crystal growth will be proportional to the square of the driving force, which was found to hold experimentally for many systems. At high supersaturation, the rate is predicted to be proportional to the driving force.

By use of the proper experimental conditions and fitting the four models described earlier, it may be possible to arrive at a reasonable mechanistic interpretation of the experimental data. As an example, the crystal growth kinetics of theophylline monohydrate was studied by Rodriguez-Hornedo