where G is the linear growth rate, L is the crystal length, and t is time. There are four models that describe crystal growth, which are based on which step is considered as rate-limiting:

1. Solute transport within the bulk solution phase to the crystal surface
2. Uniform attachment of growth units (i.e., solute molecules) to a surface that is rough on a molecular scale
3. Nucleation of two-dimensional clusters on the surface, which expand and merge to form new layers
4. Spreading of layers from a screw-lattice dislocation that acts as a continuous source of steps

Diffusion-Controlled Crystal Growth Theory

If the equilibrium at the crystal face is established rapidly so as not to be rate-limiting, the crystallization process would be controlled by solute transport, which is proportional to the solute concentration gradient across the stagnant layer ($c_t - c_s$). The rate of crystallization could be modeled using Ficks' law of diffusion and is given by

$$G = \left(\frac{DV_m \left(c_t - c_s \right)}{h} \right) \tag{17.36}$$

where the terms of the equation were defined earlier in the section on dissolution phenomena. Note that the form of the equation describing diffusion-controlled crystal growth is analogous to the equation describing dissolution phenomena, except for inversion with respect to the direction of the solute concentration gradient. It has been shown that the width of the diffusion layer, h, is essentially nonexistent in well-stirred solutions and that the bulk of the solution in contact with the growing crystal face is not saturated but supersaturated. This would imply the presence of at least two mechanisms: diffusion across the boundary layer and reorganization of the encroaching molecule into the proper orientation for incorporation into the growing crystal lattice. As pointed out by Greco Macie and Grant (1986), the molecular mechanism is more complex than a two-stage process. However, the usefulness of this theory of crystal growth lies in the capability for measuring and reporting crystal growth rates using diffusional and mass transfer equations.

Adsorption-Layer Theory

The other three models differ in mechanism; however, they share common assumptions. Molecules arriving from the bulk solution to the crystal interface retain sufficient energy, allowing them to migrate over the crystal face. Equilibrium is established between the bulk and this loosely adsorbed layer of molecules at the surface, analogous to that found in the interfacial barrier model of dissolution. These molecules will eventually integrate into the crystal lattice in such a way so as to minimize the free energy of the system, that is, where the attractive forces are maximal. The sites of integration and the surface texture are those that differentiate the three models and will be discussed now in more detail.

Uniform attachment of growth units mechanism: This mechanism refers to the situation where there is a discontinuous process of layer-by-layer adsorption of molecules onto a crystal surface that is rough on a molecular scale. This surface roughness provides numerous nuclei for attachment of solute molecules. The crystal growth rate is proportional to the driving force:

$$G = k_5 c_t \ln\left(\frac{c_t}{c_s} \right) \tag{17.37}$$