Growth Rate Dispersion by Initial Growth Rate Distributions and Growth Rate Fluctuations

Two distinctly different mechanisms that lead to growth rate dispersion have been observed experimentally. One of the mechanisms involves an initial growth rate distribution among nuclei, while the other allows crystal growth rates to fluctuate. The model formulated in the present work includes both phenomena. Solutions to population balances in a continuous mixed-suspension, mixed-product removal continuous crystallizer and a constant-supersaturation batch crystallizer are obtained in terms of parameters characterizing the two mechanisms.

R. C. Zumstein, R. W. Rousseau
Department of Chemical Engineering
North Carolina State University
Raleigh, NC 27695

Introduction

A model relating crystal size distribution (CSD) to operating variables is necessary for the rational design and control of industrial crystallizers. Modeling the CSD in an industrial crystallizer is often complicated by the occurrence of growth rate dispersion. Simply stated, growth rate dispersion is a deviation from the ΔL law (McCabe, 1929) in which all crystals in the suspension do not grow at identical and/or constant rates even though the system conditions (temperature, supersaturation, etc.) remain constant. Growth rate dispersion differs from another form of anomalous crystal growth behavior, known as size-dependent growth, in that the difference in crystal growth rates within the suspension is not related to the size of the growing crystals. White and Wright (1971) first used the concept of growth rate dispersion to explain the increase in spread of crystal sizes during batch growth periods of sucrose crystals.

Two distinctly different mechanisms that lead to growth rate dispersion have been proposed and have experimental support. The first, which was proposed by Randolph and White (1977), assumes that all crystals have the same time-averaged growth rate, but that individual crystal growth rates fluctuate during growth periods. Evidence of random fluctuations in growth rates has been reported by Lui *et al.* (1971), who found growth rates on the faces of magnesium sulfate heptahydrate fluctuate as much as 10%, and by Human *et al.* (1982), who observed the growth rate randomly fluctuating on different faces of potassium alum. The second proposed mechanism for growth rate dispersion assumes that crystals are born with a characteristic distribution of growth rates, but that individual crystals retain a constant growth rate throughout their residence in a crystallizer. This mechanism is supported by the findings of Berglund and Larson (1982) on citric acid, Berglund *et al.* (1983) on potassium nitrate, and Garside and Ristic (1983) and Blem and Ramanarayanan (1986) on ammonium dihydrogen phosphate. All of these studies found nuclei to have a distribution of growth rates and individual crystals to have constant growth rates.

The surface integration step for crystal growth is thought to be the primary factor in both mechanisms of growth rate of dispersion, and the Burton-Cabrera-Frank (BCF) growth theory (Burton et al., 1951) is often used to provide a qualitative explanation of the growth rate dispersion phenomenon. From the BCF theory, the growth rate of a crystal face is dependent on the number, sign, and location of screw dislocations on the surface of a growing crystal. Collisions of crystals with each other and crystallizer internals result in changes in the dislocation network of a crystal, and lead to the random fluctuation of growth rates. Changes in the dislocation networks also occur simply due to the imperfect growth of crystal faces. A distribution of growth rates is a result of the varying dislocation networks and densities among nuclei and seed crystals.

Although evidence for both mechanisms of growth rate dispersion exists, separate mathematical models have been developed for incorporating the two mechanisms into a description of crystal populations. Random growth rate fluctuations were characterized by Randolph and White (1977) with a growth rate diffusivity parameter D_G that is representative of the magnitude of the growth rate fluctuations. This model is similar to that used to describe molecular diffusion and velocity fluctuations. Mathematical models of growth rate dispersion due only to the growth rate distribution mechanism have been developed using different methods by Janse and deJong (1976), Berglund and Larson (1984), Ramanarayanan *et al.* (1984), and Larson *et al.* (1985). All of these models characterize this mechanism of growth rate dispersion using a growth rate distribution function for crystals with mean $\bar{G}$ and variance σ_G^2.

Experimental efforts to determine the importance of the two mechanisms of growth rate dispersion have mainly been involved with the measurement of the spread in CSD during constant-supersaturation, isothermal batch crystallizations. The model for random growth rate fluctuations predicts the variance of the CSD to increase linearly with the extent of growth, while the model for a distribution of constant crystal growth rates predicts the variance to increase with the extent of growth squared. There are experimental data from batch crystallizers to support both mechanisms. The original work by White and Wright (1971) on sucrose found that the relationship between the variance and extent of growth was linear and did not depend on seed size (10 to 500 μm) or the agitation rate in the crystallizer. To support the growth rate distribution mechanism, Blem and Ramanarayanan (1986) and Ramanarayanan *et al.* (1985) have both found the variance of the CSD to increase with the extent of growth squared for contact nuclei of ammonium dihydrogen phosphate and citric acid, respectively. These results were obtained, however, from crystal growth cells in which there was no agitation. Although there is experimental support for both mechanisms, it is still unclear how crystallizing conditions affect the relative importance of the two mechanisms.

The effects of the two growth dispersion mechanisms on the CSD in a mixed-suspension, mixed-product removal (MSMPR) continuous crystallizer are also different. Random growth rate fluctuation do not affect the spread of the CSD from an MSMPR crystallizer and the resulting population density function is indistinguishable from that obtained assuming applicability of the ΔL law. However, growth rate fluctuations do increase the mean crystal size from that which is expected from the ΔL law. The CSD from a continuous crystallizer is noticeably affected by a distribution of constant crystal growth rates for the nuclei. This mechanism causes curvature in plots of the log of crystal population density vs. crystal size that had previously been attributed to size-dependent growth. Recent work by Girolami and Rousseau (1985) showed that the relative importance of actual size-dependent growth is insignificant in comparison with growth rate dispersion.

The objective of the present study was to develop a mathematical model that characterizes, in terms of the growth dispersion parameters, the effects of both growth rate dispersion mechanisms on the CSD in batch and continuous crystallizers. From the model, the relative importance of each mechanism can be determined in the analysis of CSD data. More important, the model can be used to isolate factors that influence growth rate dispersion and it would be a rational way of scaling up laboratory data in crystallizer design. The model developed was based on the concept that crystals are introduced into the system with a distribution of time-averaged growth rates and, due to the changes in the dislocation networks of the crystals, individual crystal growth rates fluctuate about their original values during the growth period.

Population Density Function

The first step in mathematically describing the CSD in a crystallizer is to define a population density function n such that the number of crystals between sizes L_1 and L_2 is

$$N(L_1, L_2) = V_T \int_{L_1}^{L_2} n \, dL \tag{1}$$

The above definition assumes that crystals are so numerous within the suspension that the CSD may be expressed as a continuous function. As a necessity for predicting the CSD, a population balance must be solved for the crystallizer. In general, a macroscopic population balance for a well-mixed crystallizer is given by Randolph and Larson (1971) as

$$\frac{\partial n}{\partial t} + n \frac{d(\log V_T)}{dt} = B - D - \sum_k \frac{Q_k n_k}{V_T} - \nabla \cdot \hat{N}_L \tag{2}$$

where B and D are birth and death functions describing the population, Q_k is the volumetric flow rate of stream k with population density n_k, and $\hat{N}_L$ is the population flux along the internal coordinate L. As given by Randolph and White (1977), the internal flux vector written to include random growth rate fluctuations is

$$\hat{N}_L = Gn - D_G \frac{\partial n}{\partial L} \tag{3}$$

where G is the time-averaged growth rate of the crystals, and D_G is known as the growth rate diffusivity. The growth rate diffusivity represents the magnitude of the growth rate fluctuations. The overall population flux due to the fluctuations is also dependent on the population size gradient $\partial n/\partial L$. The general macroscopic population balance on a crystallizer in which random growth rate fluctuations occur but all crystals have the same time-averaged growth rate is

$$\frac{\partial n}{\partial t} + n \frac{d(\log V_T)}{dt} = B - D - \sum_k \frac{Q_k n_k}{V_T} - \frac{\partial (Gn)}{\partial L} + \frac{\partial \left(D_G \frac{\partial n}{\partial L} \right)}{\partial L} \tag{4}$$

The population density function n can also be defined in terms of probability theory as

$$n(L) = N_T f(L) \tag{5}$$

where N_T is the total number of crystals per unit volume in the crystallizer and $f(L)$ is the probability density function for the random variable L. Since probability density functions are normalized, $f(L)$ can also be referred to as the normalized population density function. When there exists a distribution of growth rates as well as a distribution of sizes, a joint probability density function $f(G, L)$ for the random variables G and L is used to describe the crystal population. By definition, the joint probability density function is related to the normalized population density function by

$$f(L) = \int_0^\infty f(G, L) dG \tag{6}$$

and $f(L)$ becomes a marginal density function of the random variable L. Analogous to the above definition, a marginal density function $f(G)$ for the random growth rate variable G is defined by the expression

$$f(G) = \int_0^\infty f(G, L)\, dL \tag{7}$$

so that $f(G)$ is the growth rate distribution function for the population. Also by definition, the probability density function for all crystal sizes that have a growth rate G is

$$f(L/G) = \frac{f(G, L)}{f(G)} \tag{8}$$

where $f(L/G)$ is known as the conditional probability density function of L at a given G.

The population balance presented by Eq. 4 is applicable only when all crystals within the crystallizer have the same time-averaged growth rate. When a distribution of time-averaged growth rates exists, a population balance, analogous to that which gave Eq. 4, can be written for crystals with time-averaged growth rate G using the conditional density function $f(L/G)$:

$$\frac{\partial f(L/G)}{\partial t} + f(L/G)\,\frac{\partial(\log V_T)}{\partial t} = B(G) - D(G) - \sum_k \frac{Q_k f_k(L/G)}{V_T} - \frac{\partial[G f(L/G)]}{\partial L} + \frac{\partial D_G \dfrac{\partial f(L/G)}{\partial L}}{\partial L} \tag{9}$$

where $B(G)$ and $D(G)$ are the birth and death functions describing the population with growth rate G. The CSD within a crystallizer described by the population density function can therefore be determined by the solution of the conditional population balance, Eq. 9, and the application of Eqs. 5, 6, and 8:

$$n(L) = N_T \int_0^\infty f(G)\, f(L/G)\, dG \tag{10}$$

so that the entire CSD is dependent on the distribution of growth rates for all crystals.

The moments of the population density function are often used to characterize the CSD. The jth moment about the origin of the population density function is defined by

$$m_j = \int_0^\infty L^j n(L)\, dL \quad j = 0, 1, 2, \ldots, \tag{11}$$

The jth moment about the origin of the conditional probability density function is

$$\overline{m}_j(G) = \int_0^\infty L^j f(L/G)\, dL \quad j = 0, 1, 2, \ldots \tag{12}$$

where $\overline{m}_j(G)$ is the jth normalized moment for all crystals with time-averaged growth rate G. The relationship between the conditional population moments and the moments of the entire CSD can be found by first combining Eqs. 6 and 11 to give

$$m_j = N_T \int_0^\infty L^j \int_0^\infty f(L, G)\, dG dL \tag{13}$$

Equation 8 can then be used to eliminate the joint density function in favor of the conditional density function to give

$$m_j = N_T \int_0^\infty L^j \int_0^\infty f(G) f(L/G)\, dG dL \tag{14}$$

Rearranging Eq. 14 and interchanging the order of integration, the jth moment of the population is

$$m_j = N_T \int_0^\infty f(G) \int_0^\infty L^j f(L/G)\, dL dG \tag{15}$$

$$= N_T \int_0^\infty f(G) \overline{m}_j(G)\, dG \tag{16}$$

The first four moments are related to the total number, length, area, and volume of crystals. Two important examples of the use of moments are the population-weighted mean crystal size

$$\overline{L} = \frac{m_1}{m_0} \tag{17}$$

and the variance of the CSD about that mean.

$$\sigma_L^2 = \frac{m_2 - m_1^2/m_0}{m_0} \tag{18}$$

Mathematical Models of Crystallizers

The model of growth rate dispersion depicts crystals as entering or born within the crystallizer with a distribution of time-averaged growth rates and, due to changes in the dislocation network upon the crystal surfaces, individual crystal growth rates fluctuate about original values. The model also assumes that both the time-averaged growth rate G and the growth rate diffusivity D_G are independent of crystal size. The experimental observations of White and Wright (1971) on sucrose justify this additional assumption. However, the growth rate diffusivity parameter may be dependent on the time-averaged growth rate, as suggested by Randolph and White (1977).

Batch crystallization

The conditional population balance given by Eq. 9 can be simplified to describe an isothermal batch crystallizer operating with constant supersaturation and volume, and with negligible crystal breakage and nucleation to give

$$\frac{\partial f(L/G)}{\partial t} + G\frac{\partial f(L/G)}{\partial L} = D_G \frac{\partial^2 f(L/G)}{\partial L^2} \tag{19}$$

where $f(L/G)$ is the conditional density function defined by Eq. 8. Operation of a batch crystallizer satisfying the above conditions has been achieved experimentally by White and Wright.

As suggested earlier, moments can be used to characterize the CSD, and therefore they can be used to demonstrate the effect of both growth rate mechanisms on the CSD. Randolph and White demonstrated how the macroscopic population balance, given by Eq. 4, could be transformed to give a set of moment equations for a system with random growth rate fluctuations, but having a single time-average growth rate for all crystals. Analogous to this approach, the conditional population balance given by Eq. 19 can be transformed to give the following set of conditional moment equations:

$$\frac{d\overline{m}_0(G)}{dt} = 0 \tag{20a}$$

$$\frac{d\overline{m}_1(G)}{dt} = G\overline{m}_0(G) \tag{20b}$$

$$\frac{d\overline{m}_2(G)}{dt} = 2G\overline{m}_1(G) + 2D_G\overline{m}_0(G) \tag{20c}$$

$$\frac{d\overline{m}_j(G)}{dt} = jG\overline{m}_{j-1}(G) + j(j-1)D_G\overline{m}_{j-2}(G) \tag{20d}$$

where $\overline{m}_j(G)$ is the jth moment of the normalized population of crystals having time-averaged growth rate G defined by Eq. 12. The solution to this set of ordinary differential equations requires stipulation of the initial conditions of the moments. For a seed population with mean crystal size $\overline{L}_i$ and variance $\sigma^2_{L_i}$, the initial conditions for the first three moments are

$$\overline{m}'_0(G) = 1 \tag{21a}$$

$$\overline{m}'_1(G) = \overline{L}_i \tag{21b}$$

$$\overline{m}'_2(G) = \sigma^2_{L_i} + \overline{L}^2_i \tag{21c}$$

The solutions to Eqs. 20 and 21 are given by

$$\overline{m}_0(G) = 1 \tag{22a}$$

$$\overline{m}_1(G) = \overline{L}_i + Gt \tag{22b}$$

$$\overline{m}_2(G) = \sigma^2_{L_i} + \overline{L}^2_i + 2Gt\overline{L}_i + G^2t^2 + 2D_Gt \tag{22c}$$

Assuming that the initial size distribution of all crystals is independent of growth rate, Eqs. 22a–c can be substituted into Eq. 16 to determine the moments of the entire crystal population within the crystallizer:

$$m_0 = N_T \tag{23a}$$

$$m_1 = N_T[\overline{L}_i + \overline{G}t] \tag{23b}$$

$$m_2 = N_T\left[\sigma^2_{L_i} + \overline{L}^2_i + 2\overline{G}t\overline{L}_i + \sigma^2_Gt^2 + \overline{G}^2t^2 + 2\int_0^\infty f(G)D_G\,dG\right] \tag{23c}$$

where $\overline{G}$ and σ^2_G are the mean and variance of the growth rate distribution. Using these expressions for the moments, the time dependences of the mean and variance of the CSD in the batch crystallizer are therefore:

$$\overline{L}(t) = \overline{L}_i + \overline{G}t \tag{24}$$

$$\sigma^2_L(t) = \sigma^2_{L_i} + \sigma^2_Gt^2 + 2t\int_0^\infty f(G)D_G dG \tag{25}$$

If D_G is not a function of growth rate, the final term in Eq. 25 reduces to $2D_Gt$. If there is no distribution of growth rates, σ^2_G is zero; on the other hand, the parameter D_G is zero when no fluctuations in crystal growth rates occur. In other words, Eq. 25 reduces to the expression given by Randolph and White for growth rate dispersion due to the random growth rate fluctuation mechanism, and it also reduces to the expression given by Ramanarayanan *et al.* (1985) for systems in which only the growth rate distribution mechanism exists.

Continuous MSMPR crystallization

For a continuous, steady-state MSMPR crystallizer with a clear feed, the conditional population balance given by Eq. 9 can be reduced to

$$G\frac{df(L/G)}{dL} - D_G\frac{d^2f(L/G)}{dL^2} = -\frac{f(L/G)}{\tau} \tag{26}$$

where τ is the mean residence time of the crystals in the crystallizer. The solution to this second-order ordinary differential equation requires the stipulation of two boundary conditions. One boundary condition simply requires the conditional population density to be finite as $L \longrightarrow \infty$. The other boundary condition is associated with nucleation. In general, it is assumed that nuclei are formed at various initial sizes according to a distribution function $f(L_i)$. Often, for simplicity, nuclei are assumed to be formed at zero size. The population density function for this simpler case of nucleation will be determined first, followed by the general case.

Nucleation at Zero Size. The solution to Eq. 26 for birth occurring at zero size with nucleation rate B^0 is

$$f(L/G) = C\exp\left(-\frac{SL}{G\tau}\right) \tag{27}$$

where C is a constant of integration and

$$S = \left(\frac{\tau G^2}{2D_G}\right)\left[\left(1 + \frac{4D_G}{\tau G^2}\right)^{1/2} - 1\right] \tag{28}$$

The parameter S can be shown to be bounded between 0 and 1. Since $f(L/G)$ is a normalized probability density function, the integral over all possible sizes must be equal to unity. This constraint requires the integration constant C to be equal to $S/G\tau$. Using Eq. 10, the resulting population density function is

$$n(L) = N_T\int_0^\infty \frac{S}{G\tau}f(G)\exp\left(-\frac{SL}{G\tau}\right)dG \tag{29}$$

where $f(G)$ represents the distribution function for all crystals within the crystallizer. Equation 29 reduces to the expression given by Larson *et al.* (1985) for the special case of no random growth rate fluctuations. The distribution of nuclei growth rates is not the same as that for all crystals because of the residence time distribution within the crystallizer. A conditional probability density function for the nuclei growth rate distribution can be defined similarly to the conditional population density function of Eq. 8:

$$f(G/L = 0) = \frac{f(L = 0, G)}{f(L = 0)} \tag{30}$$

Substituting the solution of the population balance, Eq. 29, into this definition, the normalized distribution function for the nuclei growth rates $f(G/L = 0)$ is related to the distribution function for all crystals in the suspension $f(G)$ by

$$f(G/L = 0) = \frac{\dfrac{Sf(G)}{G}}{\displaystyle\int_0^\infty \frac{Sf(G)}{G}\,dG} \tag{31}$$

Noting that the total number of crystals in the crystallizer N_T must be equal to the integral over all possible sizes of the population density function given by Eq. 29, it can be shown using Eq. 31 that

$$\int_0^\infty \frac{Sf(G)}{G}\,dG = \frac{1}{\displaystyle\int_0^\infty \frac{Gf(G/L = 0)}{S}\,dG} \tag{32}$$

Defining the nucleation rate as $B^0 \equiv N_T/\tau$, the population density function for an MSMPR crystallizer in which both mechanisms of growth rate dispersion occur can be written as

$$n(L) = \frac{B^0}{\displaystyle\int_0^\infty \frac{Gf(G/L = 0)}{S}\,dG} \times \int_0^\infty f(G/L = 0) \exp\left(-\frac{SL}{G\tau}\right) dG \tag{33}$$

A Distribution of Nuclei Sizes. For the general case of nuclei being formed at a finite distribution of sizes, a definition of a new joint probability density function $f(L, G, L_i)$ is required, which includes the three random variables, L, G, and L_i. The population density function is related to this new normalized joint density function by

$$n(L) = N_T \int_0^L \int_0^\infty f(L, G, L_i)\, dG dL_i \tag{34}$$

A conditional probability density function for the random variable L at given values G and L_i is related to the new joint density function by

$$f(L/G/L_i) = \frac{f(L, G, L_i)}{f(G)f(L_i)} \tag{35}$$

where $f(G)$ is the growth rate distribution function for all the crystals in the crystallizer, and $f(L_i)$ is the initial size distribution of all crystals in the crystallizer. The expression given by Eq. 35 assumes that the growth rate G and initial size L_i of a crystal are independent random variables.

Analogous to the previous derivation of equations describing an MSMPR crystallizer, the conditional population balance for crystals with time-averaged growth rates G that were born at size L_i is

$$G\frac{df(L/G/L_i)}{dL} - D_G\frac{d^2f(L/G/L_i)}{dL^2} = -\frac{f(L/G/L_i)}{\tau} \tag{36}$$

Solving Eq. 36 for the conditional density function $f(L/G/L_i)$ and following a method similar to that which gave Eq. 29 from Eq. 27, the population density function is

$$n(L) = N_T \int_0^L \int_0^\infty f(L_i)f(G)\frac{S}{G\tau} \times \exp\cdot\left[-\frac{S(L - L_i)}{G\tau}\right] dGdL_i \tag{37}$$

where S is given by Eq. 28. Equation 37 reduces to the expression given by Berglund and Larson (1984) when random growth rate fluctuations are neglected. The growth rate distribution for all crystals can be related to a growth rate distribution function $f(G/L = L_i/L_i)$ of the nuclei born at size L_i by an expression similar to Eq. 31 and the population density function can be rewritten as

$$n(L) = \frac{B^0 \displaystyle\int_0^L \int_0^\infty f(L_i) f(G/L = L_i/L_i) \exp\left[-\frac{S(L - L_i)}{G\tau}\right] dGdL_i}{\displaystyle\int_0^\infty \frac{Gf(G/L = L_i/L_i)}{S}\,dG} \tag{38}$$

Application of Eq. 38 to predict the CSD within an MSMPR crystallizer requires knowledge of both the initial size and growth rate distribution functions for nuclei. Equation 38 reduces to Eq. 33 for the case of nuclei all forming at zero size.

Discussion

Equations 24 and 25 suggest that the parameters for the growth rate dispersion mechanisms can be determined by monitoring the CSD during batch crystallization with constant growth conditions. If the assumptions of the model are valid, particularly the one requiring the absence of size-dependent growth, a plot of the mean of the CSD $\bar{L}$ vs. growth period t should result in a straight line with a slope equal to the mean of the growth rate distribution $\bar{G}$. The two growth rate dispersion parameters, σ_G^2 and D_G, can then be determined by plotting the variance σ_L^2 of the CSD vs. t. This plot can result in four qualitatively different curves, as shown in Figure 1, with the differences depending on the magnitude and mechanism of growth rate dispersion. Curve *1* is representative of the case of no growth rate dispersion, so that there is no increase in the spread of the CSD; both σ_G^2 and D_G are zero for this case. When the spread of the CSD constantly increases during growth, as shown by curve *2*, only random growth rate fluctuations contribute to the growth rate dispersion. The existence of a distribution of crystal growth rates causes upward curvature in the plot. When growth rate dispersion is due only to a distribution of growth rates, curvature similar to that of curve *3*, where the variance of the CSD increases with the increase in growth period squared is expected. Curve *4* represents the typical shape of this plot when both mechanisms for growth rate dispersion occur. In general, the remaining two growth rate dispersion parameters must be estimated by fitting a parabolic curve through a σ_L^2 vs. t plot. Equation 25 can then be used to estimate σ_G^2 and D_G from the regressed coefficients. However, the growth rate diffusivity pa-

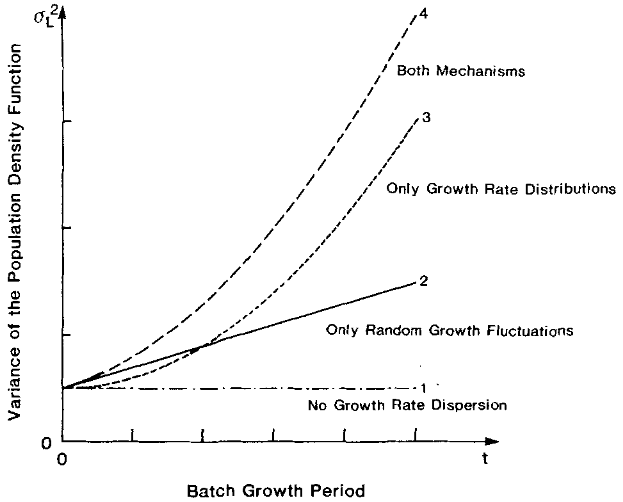

Figure 1. Effect of growth rate dispersion mechanisms on the spread of CSD during batch crystallization.

rameter D_G can only be obtained when its dependence on growth rate is known.

Experimental evidence to support each individual growth rate dispersion mechanism has been reported. Equations 24 and 25 can be combined to express the general relationship between the variance of the CSD and the extent of growth $\Delta\bar{L}$, defined as $\bar{L}(t) - \bar{L}_i$, as

$$\sigma_L^2(\Delta\bar{L}) = \sigma_i^2 + 2\frac{D_G}{\bar{G}}(\Delta\bar{L}) + \frac{\sigma_G^2}{\bar{G}^2}(\Delta\bar{L})^2 \qquad (39)$$

with D_G assumed to be independent of growth rate. Blem and Ramanarayanan (1986), and Ramanarayanan *et al.* (1985) have both found that a distribution of growth rates exists for contact nuclei and that the variance of the CSD increases with the extent of growth squared. These results follow the behavior of curve *3* in Figure 1 and indicate that there was negligible fluctuation of individual growth rates, so that D_G is essentially zero. It should be pointed out that these results were obtained on nuclei in a stagnant growth cell. No agitation was provided and no collisions among crystals occurred, thereby eliminating two major potential causes of random growth rate fluctuations. On the other hand, experimental results similar to curve *2* in Figure 1 have been reported by White and Wright (1971). Their results indicate that the seed crystals they used all had the same time-averaged growth rate, so that σ_G was zero. There was no apparent dependence of their results on mechanical agitation. This conclusion is questionable since even in the absence of a mechanical stirrer, vigorous agitation of the suspension was provided by the boiling action in the vessel. No experimental evidence has yet been reported to confirm the coexistence of both mechanisms for growth rate dispersion during batch crystallization.

The effect of each growth rate dispersion mechanisms on the CSD from an MSMPR crystallizer is presented in Figure 2. Equation 33 was used to generate Figure 2 and a gamma distribution function with mean $\bar{G}_i$ and variance σ_{Gi}^2 was used to describe the growth rate distribution function of nuclei. As introduced earlier, random growth rate fluctuations do not alter the form of the CSD but do increase the mean crystal size from that expected for crystal growth following the ΔL law. A distribution of crystal growth rates produces curvature in the population plot (ln n vs. L) similar to that of size-dependent growth. Figure 3 demonstrates the ability of random growth rate fluctuations to dominate and overshadow the effects of the growth rate distribution mechanism. Therefore, both mechanisms for growth rate dispersion can be present in an MSMPR crystallizer, but due to the magnitude of the random growth rate fluctuations, the population density plot could have the appearance associated with the ΔL law of crystal growth. This result is quite different from batch crystallization, where both mechanisms could easily be observed if they were occurring. Also, this result indicates that the method suggested by Randolph and Larson (1971) for determining nucleation and growth rates from an MSMPR crystallizer cannot distinguish between systems following the ΔL law and those exhibiting growth rate dispersion due to growth rate fluctuations. The validity of the kinetic expressions determined from MSMPR crystallizers is therefore uncertain, especially for systems in which growth rate dispersion is known to occur.

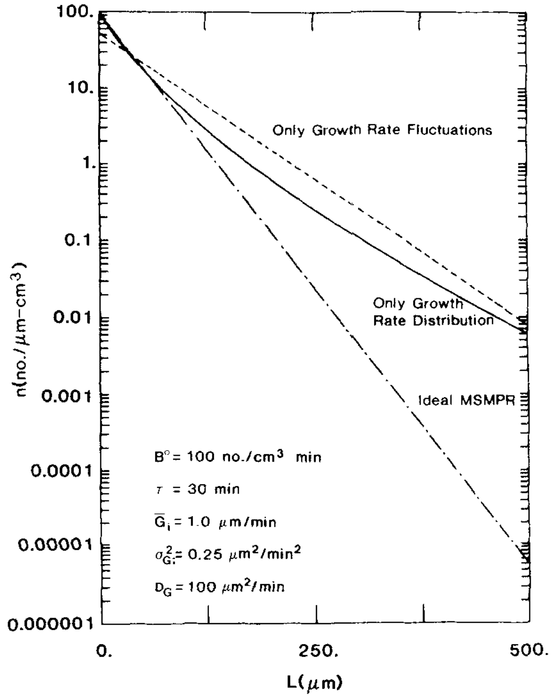

Figure 2. Effect of individual growth rate dispersion mechanisms on CSD in an MSMPR crystallizer.

Based on Eq. 33, using a gamma distribution function with mean $\bar{G}_i$ and variance $\sigma_{G_i}^2$ for $f(G/L = 0)$.

The size distribution function of nuclei formed in an MSMPR crystallizer must be known in order to use Eq. 38 and thereby determine the population density function for the general MSMPR crystallizer. Contact nucleation studies by Cise and Randolph (1972), Randolph and Sikdar (1976), Garside and Jancic (1976), and Garside *et al.* (1979) have all found that the size distribution function for nuclei is best described by an exponential distribution function. Berglund and Larson (1982) and Berglund *et al.* (1983) reported results contrary to the above

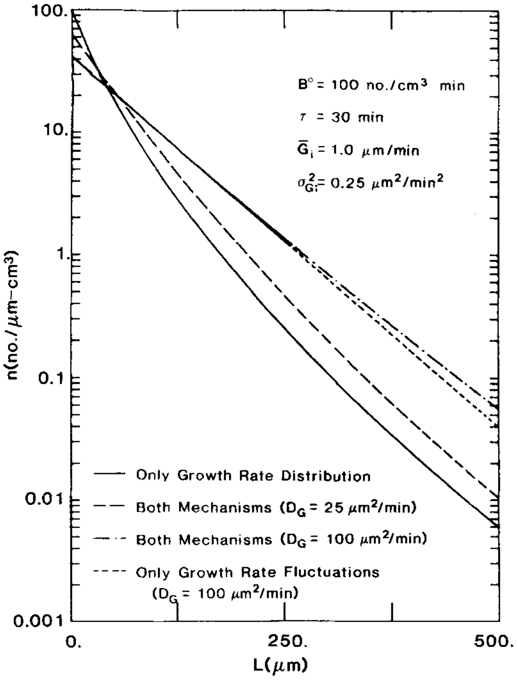

Figure 3. Effect of random growth rate fluctuations on CSD in an MSMPR crystallizer.

Based on Eq. 33, using a gamma distribution function with mean $\bar{G}_i$ and variance $\sigma^2_{G_i}$ for $f(G/L = 0)$.

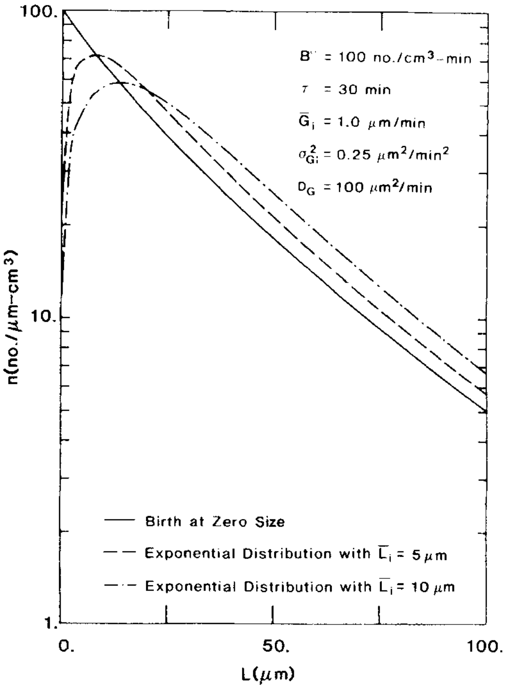

Figure 4. Effect of an initial size distribution for nuclei [*f*(L_i)] on CSD in an MSMPR crystallizer.

Based on Eq. 38, using a gamma distribution function with mean $\bar{G}_i$ and variance $\sigma^2_{G_i}$ for $f(G/L = L_i/L_i)$.

observations; they found that the initial size of contact nuclei is best described by a gamma distribution function. As explained by Berglund and Larson (1984), the experimental technique used to measure the initial size distribution in the latter two studies was not sensitive enough to determine thoroughly the distribution below about 2 μm or to reject the hypothesis that the size of nuclei follows an exponential distribution function.

Assuming an exponential distribution function to characterize the initial nuclei size, the effect on the CSD of the mean initial size is shown in Figure 4. The initial size distribution affects the CSD by causing a downward curvature of the population plot at sizes less than the mean nuclei size. Berglund and Larson (1984) presented similar results using a gamma distribution function to characterize nuclei sizes. The only deviations from linearity of the population plot in these low size ranges that have been experimentally observed is an upward curvature as crystal size decreases. These results suggest that the mean of the nuclei size distribution is so small that the effect of the initial size distribution is unobservable even with electronic particle sizing techniques. Figure 4 demonstrates that if the mean nuclei size is small (<5 μm), a distribution of nuclei sizes has little effect on the CSD, so that assuming nucleation to occur at zero size is an excellent approximation.

As pointed out by Janse and deJong (1976), growth rate dispersion, due to a distribution of crystal growth rates, causes curvature in the population plot and the appearance of size-dependent growth. This apparent size-dependent growth can be described through the use of a conditional growth rate distribution function, defined analogously to Eq. 30 as

$$f(G/L) = \frac{f(L, G)}{f(L)} \tag{40}$$

where $f(G/L)$ is the growth rate distribution of crystals at size L. Similar to Eq. 31, the conditional growth rate distribution function for an MSMPR crystallizer with both growth rate dispersion mechanisms is

$$f(G/L) = \frac{f(G/L = 0)\exp\left(-\dfrac{SL}{G\tau}\right)}{\displaystyle\int_0^\infty f(G/L = 0)\exp\left(-\frac{SL}{G\tau}\right) dG} \tag{41}$$

where $f(G/L = 0)$ is the growth rate distribution for the nuclei that are born at zero size. The mean growth rate of crystals varies with crystal size by

$$\bar{G}(L) = \int_0^\infty G f(G/L)\, dG \tag{42}$$

and the variance of the conditional growth rate distribution varies with size by

$$\sigma^2_G(L) = \int_0^\infty [G - \bar{G}(L)]^2 f(G/L)\, dG \tag{43}$$

Figure 5 presents the apparent size-dependent growth due to the distribution of nuclei growth rates. The increase of the mean crystal growth rate as size increases is due to faster growing crystals having a higher probability of populating the larger sizes. This increase in mean growth rate as crystal size increases is accompanied by a decrease in the variance of the conditional growth rate distribution, as shown in Figure 6. Figures 5 and 6 also show that random growth rate fluctuations decrease the apparent size-dependent growth of crystals in an MSMPR crys-

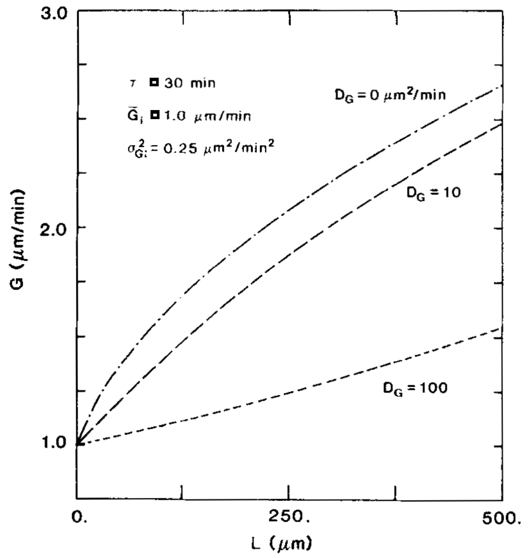

Figure 5. Apparent size-dependent crystal growth due to a distribution of growth rates.

Based on Eq. 42, using a gamma distribution function with mean $\bar{G}_i$ and variance $\sigma^2_{G_i}$ for $f(G/L = 0)$.

tallizer and are directly responsible for the decrease in curvature of the population plot as shown in Figure 3. In general, even when both growth dispersion mechanisms occur, the distribution of growth rates at large crystal sizes has a smaller spread but larger mean than crystals at small sizes.

The shapes of the curves shown in Figures 5 and 6 are highly dependent on the distribution function used to characterize the nuclei growth rates. A gamma distribution function has been used in the present work, and a majority of the experimental data indicate that it is a reasonable choice. Other distribution functions have been suggested; for example, Janse and deJong (1976) used an inverse gamma distribution function and found a linear relationship between the mean growth rate and crystal size. Moreover, the gamma distribution function does not allow zero growth rates, which have been observed in some systems, and it does not reproduce the simultaneous exhibition of steep curvature in population density plots at small sizes and linearity at large sizes that has been observed in some systems. Growth rate dispersion due only to growth following a gamma distribution function results in modest curvature of the entire population density plot. Inclusion of zero growth rates for nuclei in the growth distribution function would result in an increase in curvature of the population plot at small crystal sizes.

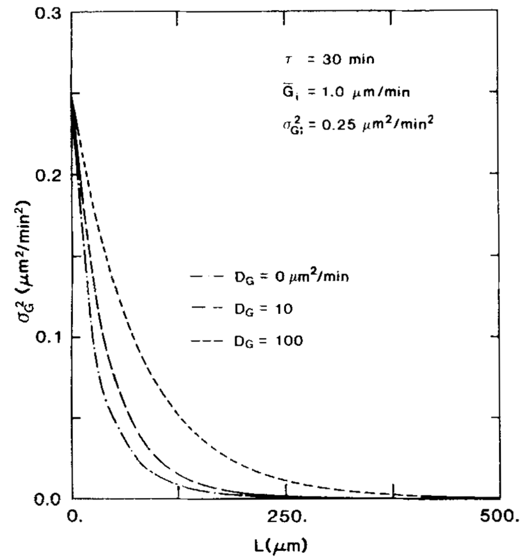

Figure 6. Effect of growth rate dispersion on the spread of crystal growth rates at different sizes.

Based on Eq. 43, using a gamma distribution function with mean $\bar{G}_i$ and variance $\sigma^2_{G_i}$ for $f(G/L = 0)$.

Conclusions

A model that shows the effects of two growth rate dispersion mechanisms on the product CSD obtained from batch and continuous crystallizers has been derived. Both the growth rate distribution and random growth rate fluctuation mechanisms cause an increase in the spread of the CSD obtained from a batch crystallizer and can be separately observed experimentally by monitoring the increase in the variance of the CSD during growth periods. However, only the growth rate distribution mechanism can be experimentally observed in a continuous crystallizer since it causes an increase in the spread of the CSD, which is seen as upward curvature in the population plot. Random growth rate fluctuations may damp out the effect of the growth rate distribution and thereby cause growth rate dispersion to be unobservable in a continuous crystallizer.

The addition to the model of a size distribution function that characterizes nuclei formed in an MSMPR crystallizer does not explain the upward curvature in the population density plot that has been observed at small sizes for some systems. In fact, the distribution function causes downward curvature in the population plot. As downward curvature has never been observed experimentally, the mean nuclei size must be much smaller than the smallest size measured. This indicates that the assumption of birth at zero size is a very good approximation.

The growth distribution function for crystals at a given size in an MSMPR crystallizer differs from that of the nuclei. In particular, the spread of growth rates at a particular crystal size decreases rapidly as crystal size increases, while the mean growth rate increases with size and results in apparent size-dependent growth. This observation adds an additional explanation to the apparent disagreement in batch crystallization experiments on growth rate dispersion. White and Wright (1971) reported data for batch crystallization on sugar that show little if any effect of growth rate distributions, while contact nuclei studies report data that show a large effect of the initial growth rate distribution. The proposed combined mechanism can explain these seemingly contradictory results on the basis of the seed crystals used in the respective experiments: White and Wright presented results on large seed crystals, which possibly had a very small spread of growth rates so that the random fluctuation of growth rate accounted for the observed growth rate dispersion; on the other hand, the contact nucleation research showed the existence of a distribution of crystal growth rates for nuclei.

Notation

B = birth function of crystals within a crystallizer
$B(G)$ = birth function for the population with growth rate G
B^0 = crystal nucleation rate

C = constant of integration from the solution to Eq. 26
D = death function of crystals within a crystallizer
$D(G)$ = death function for the population with growth rate G
D_G = growth rate diffusivity parameter
$f(X)$ = probability density function for X
$f(X, Y)$ = joint probability density function for X and Y
$f(X/Y)$ = conditional probability density function for X given Y
$f(X, Y, Z)$ = joint probability density function for X, Y, and Z
$f(X/Y/Z)$ = conditional probability density function for X given Y and Z
G = linear time-averaged crystal growth rate
$\bar{G}$ = mean time-averaged growth rate of crystals
L = characteristic one-dimensional crystal size
$\bar{L}$ = number-weighted mean crystal size of population
$\Delta\bar{L}$ = extent of crystal growth
m_j = jth moment of population density function
$\overline{m}_j(G)$ = jth moment of conditional population density function
$N(L_1, L_2)$ = number of crystals between sizes L_1 and L_2
N_T = total number of crystals per unit volume in crystallizer
$\hat{N}_L$ = population flux along internal size coordinate
n = population density function
Q = volumetric flow rate
S = parameter, Eq. 28
t = crystallization time
σ_X^2 = variance of X distribution function
τ = suspension residence time

Subscripts

i = with respect to nuclei or seed crystals
k = properties of kth stream

Literature cited

Berglund, K. A., E. L. Kaufman, and M. A. Larson, "Growth of Contact Nuclei of Potassium Nitrate," *AIChE J.*, **25**, 867 (1983).

Berglund, K. A., and M. A. Larson, "Growth of Contact Nuclei of Citric Acid Monohydrate," *AIChE Symp. Ser.*, **78**(215), 9 (1982).

———, "Modeling of Growth Rate Dispersion of Citric Acid Monohydrate in Continuous Crystallizers," *AIChE J.*, **30**, 280 (1984).

Blem, K. E., and K. A. Ramanarayanan, "Generation and Growth of Secondary Ammonium Dihydrogen Phosphate Nuclei," in press, *AIChE J.*, (1986).

Burton, W. K., N. Cabrera, and F. C. Frank, "The Growth of Crystals and the Equilibrium Structure of their Surfaces," *Phil. Trans. Roy. Soc.*, **243**(A866), 299 (1951).

Cise, M. D., and A. D. Randolph, "Secondary Nucleation of Potassium Sulfate in a Continuous-Flow Seeded Crystallizer," *AIChE Symp. Ser.*, **68**(121), 42 (1972).

Garside, J., and S. F. Jancic, "Growth and Dissolution of Potash Alum Crystals in the Subsieve Size Range," *AIChE J.*, **22**, 887 (1976).

Garside, J., and R. I. Ristic, "Growth Rate Dispersion Among ADP Crystals Formed by Primary Nucleation," *J. Cryst. Growth*, **61**, 215 (1983).

Garside, J., I. T. Rusli, and M. A. Larson, "Origin and Size Distribution of Secondary Nuclei," *AIChE J.*, **25**, 57 (1979).

Girolami, M. W., and R. W. Rousseau, "Size-Dependent Crystal Growth: A Manifestation of Growth Rate Dispersion in the Potassium Alum-Water System," *AIChE J.*, **31**, 1821 (1985).

Human, H. J., W. J. P. van Enckevork, and P. Bennema, "Spread in Growth Rates on the (111), (100), and (110) faces of Potash Alum Growing from Aqueous Solutions," *Industrial Crystallization 81*, S. J. Jancic and E. J. deJong, eds., North-Holland, Amsterdam, 387 (1982).

Janse, A. H., and E. J. deJong, "The Occurrence of Growth Dispersion and Its Consequences," *Industrial Crytallization 75*, J. W. Mullin, Ed., Plenum, New York, 145, (1976).

Larson, M. A., E. T. White, K. A. Ramanarayanan, and K. A. Berglund, "Growth Rate Dispersion in MSMPR Crystallizer," *AIChE J.*, **31**, 90 (1985).

Lui, C. Y., H. S. Tsuei, and G. R. Youngquist, "Crystal Growth from Solution," *Chem. Eng. Prog. Symp. Ser.*, **67**(110), 43 (1971).

McCabe, W. L., "Crystal Growth in Aqueous Solutions," *Ind. Eng. Chem.*, **21**, 30 (1929).

Ramanarayanan, K. A., K. Athreya, and M. A. Larson, "Statistical-Mathematical Modeling of CSD in Continuous and Batch Crystallizer," *AIChE Symp. Ser.*, **80**(240), 76 (1984).

Ramanarayanan, K. A., K. A. Berglund, and M. A. Larson, "Growth Rate Dispersion in Batch Crystallizers," *Chem. Eng. Sci.*, **40**, 1604 (1985).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York (1971).

Randolph, A. D., and S. K. Sikdar, "Creation and Survival of Secondary Crystal Nuclei: The Potassium Sulfate-Water System," *Ind. Eng. Chem. Fundam.*, **15**(1), 64 (1976).

Randolph, A. D., and E. T. White, "Modeling Size Dispersion in the Prediction of Crystal Size Distribution," *Chem. Eng. Sci.*, **32**, 1067 (1977).

White, E. T., and P. G. Wright, "Magnitude of Size Dispersion Effects in Crystallization," *Chem. Eng. Prog. Symp. Ser.*, **67**(110), 81 (1971).

Manuscript received Jan. 29, 1986, and revision received Apr. 24, 1986.