# Growth Rate Dispersion in MSMPR Crystallizers

A model is presented which relates the crystal size distribution (CSD) from a mixed-suspension, mixed-product-removal (MSMPR) crystallizer to the distribution of growth rates. This model is based on the assumption that individual contact nuclei have some inherent growth rate which remains constant, but the growth rate may vary from crystal to crystal. The crystal size distribution can be calculated from prior knowledge of the growth rate distribution. Even a limited knowledge of only the coefficient of variation and the mean growth rate permits an approximation of the expected crystal size distribution. Conversely, estimates of the mean and variance of the growth rate distribution can be determined from the moments of the CSD from an MSMPR crystallizer.

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## SCOPE

Numerous bench-scale mixed-suspension, mixed-product-removal (MSMPR) crystallizer experiments have been performed to determine nucleation and growth kinetics. The population balance analysis for MSMPR crystallizers presented by Randolph and Larson (1971) stated that a semi-logarithmic population density vs. crystal size plot should be linear. From this plot the growth rate can be determined from the slope and the nucleation rate from both the slope and intercept. Therefore, it is important that the plot is linear to establish kinetics.

Many of the MSMPR crystallizer studies have reported curvature at smaller sizes ($<50 \times 10^{-6}$ m). In recent work Berglund and Larson (1984) demonstrated that the cause of this curvature in contact nucleation is most likely due to growth rate dispersion, wherein each crystal has some inherent growth rate but different crystals have different growth rates. These growth rates have a distribution which must be determined to establish the kinetics of the system under study.

## CONCLUSIONS AND SIGNIFICANCE

A technique has been presented by which the mean and variance of the growth rate distribution (GRD) can be calculated from the crystal size distribution (CSD) of an MSMPR crystallizer. Conversely, the CSD may be predicted by prior knowledge of the GRD.

In analyses of the normal, gamma, and inverse gamma distributions for the GRD it was shown similar results are predicted for the CSD. This indicates that the exact distribution which represents the GRD does not have to be known to calculate the mean and variance of the GRD, provided that the model presented by Berglund and Larson (1984) holds.

In addition, a procedure for calculating the moments of the CSD from the moments of the GRD is presented. This procedure has an analytic solution for the inverse gamma distribution but requires a numerical solution for other distributions.

### INTRODUCTION

The crystal size distribution (CSD) on a population basis obtained from a mixed-suspension, mixed-product-removal (MSMPR) crystallizer has been shown to be

$$n(l) = n^0 \exp(-l/g\tau) \qquad (1)$$

when the growth rate is constant for all crystals (Randolph and Larson, 1971). This has been demonstrated both theoretically and experimentally for a variety of systems. However, in many instances, a departure from this ideal model has been observed. For example, the $K_2SO_4$-$H_2O$ system deviates from this model in the entire range of the crystal size distribution. A much more common phenomenon is the agreement of the experimental data with the model in the intermediate and large sizes, but marked deviations in the very small size range ($<50$ $\mu$m). These deviations almost always show orders of magnitude of crystals present in excess of those predicted by the ideal MSMPR model for the small size range approaching nuclei size.

This anomalous behavior has been attributed to size-dependent growth, classification in the crystallizer, or growth rate dispersion

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in the observed size range. In many studies all of these causes have been shown to exist to some degree. Growth rate dispersion, however, has received little attention in this context, largely because no satisfactory theory exists to explain why some crystals grow at different rates in a common environment.

White and Wright (1971) have shown that growth rate dispersion is an extremely important phenomenon affecting crystal size distribution. Using batch crystallization they showed conclusively that crystals of the same size can grow at different rates in identical environments. Moreover, there is no conclusive evidence that this phenomenon is related to crystal size.

Randolph and White (1977) assumed that growth rate distribution (GRD) is Gaussian and that every stage of a crystal's growth involved a Gaussian probability distribution. This we will denote the random fluctuation (RF) model. Under these assumptions, the expected CSD from an MSMPR crystallizer would still be represented by Eq. 1, and no evidence would exist indicating growth rate dispersion. Of course, in batch crystallization the CSD would clearly widen as growth proceeded.

Berglund et al. (1983), Berglund and Larson (1981), and Ramanarayanan (1982) have recently shown by photomicroscopic experiments that contact nuclei exhibit growth rate dispersion in systems such as $KNO_3$, citric acid, and ammonium dihydrogen phosphate. This growth rate dispersion was not appreciably dependent on nuclei size. More important, the investigators observed that individual crystals maintain a constant growth rate through their growth period. Thus, it is reasonable to postulate that an individual crystal has a characteristic growth rate for a given driving force and maintains that growth rate as it grows. This we will call the constant crystal growth (CCG) model. If this phenomenon is true for all systems in general, a non-ideal population density plot for an MSMPR crystallizer, actually a result of growth rate dispersion, could be interpreted as a result of size-dependent growth. It seems more reasonable to expect growth rate dispersion than size-dependent growth in the size range larger than that in which the Gibbs-Thomson effect is expected but smaller than sizes where the hydrodynamic effects might influence mass transfer. This range is exactly the range into which secondary nuclei are born.

Thus, two basic models can be proposed for growth rate dispersion of crystals. In the RF model developed by Randolph and White (1977), it is assumed that any crystal at any stage of growth has the possibility of a distribution of growth rates. In this assumption it is implicit that the growth rate of an individual crystal can change in some more or less random manner. The CCG model states that a distribution of crystals has a distribution of growth rates, and that as soon as a crystal is born in the distribution, it has a specific growth rate and adheres to that growth rate during its entire growth period. This paper takes the latter view, which is the one taken by Berglund and Larson (1984). Berglund and Larson (1984) also modeled an MSMPR crystallizer with growth rate dispersion using gamma distributions to characterize both the initial sizes and the growth rates of crystals. They used probability transform techniques to develop a computer solution for CSD in an MSMPR crystallizer with growth rate dispersion.

This paper presents a simpler approach starting with the ideal MSMPR equation, and accounts for the variation of growth rates among crystals. An explicit relationship between the moments of the size distribution and the moments of the growth distribution is presented, and an analytical expression is developed for the CSD and the moments of the CSD when the growth rate distribution can be characterized by what we call an inverse gamma distribution.

## THE MODEL

The following assumptions are made in developing this model:

1. The crystals are born close to zero size, and the product size is much larger than the size at which they were born.
2. The growth rate of a crystal is independent of its size.
3. The CCG model is assumed applicable.

According to the ideal MSMPR model, the population density of crystals growing with a growth rate $g_i$ is given by

$$n_i(l) = n_i^0 \exp(-l/g_i\tau) \tag{2}$$

and the number of crystals greater than size $l$ with a growth rate $g_i$ is

$$N_i(l) = B_i^0\tau \exp(-l/g_i\tau) \tag{3}$$

Since $g_i$ is a random variable independent of size $l$, the CSD of the product, $n(l)$, is merely the sum of the distributions for each individual $g_i$ given by

$$n(l) = \sum_{i=0}^{\infty} n_i(l) = \sum_{i=0}^{\infty} n_i^0 \exp(-l/g_i\tau) \tag{4}$$

Let $f_G(g)$ represent the distribution of growth rates for the crystals such that $f_G(g)dg$ is the fraction of the total number of crystals having a growth rate of $g$.

Thus, the number of crystals of size greater than $l$ with a growth rate $g$ is

$$N_g(l) = B^0\tau \exp(-l/g\tau) f_G(g)dg \tag{5}$$

where $B^0\tau$ is the total number of crystals in the crystallizer.

Further, the number of crystals greater than size $l$ with all possible growth rates is

$$N(l) = \int_0^{\infty} N_g(l) \tag{6}$$

$$= \int_0^{\infty} B^0\tau \exp(-l/g\tau) f_G(g)dg \tag{7}$$

Thus, the fraction of the total crystals greater than size $l$ is

$$F_L(l) = N(l)/B^0\tau = \int_0^{\infty} \exp(-l/g\tau) f_G(g)dg \tag{8}$$

and

$$f_L(l) = \int_0^{\infty} (1/g\tau) \exp(-l/g\tau) f_G(g)dg \tag{9}$$

is such that $f_L(l)dl$ equals the fraction of the total number of crystals in the size range $l$ to $l + dl$. From Eq. 9, knowing the growth rate distribution $f_G(g)$, the CSD $f_L(l)$ can be obtained by simple integration.

Multiplying both sides of Eq. 9 by $l^j$, integrating between 0 and $\infty$, and realizing that $g$ and $l$ are assumed to be independent,

$$\int_0^{\infty} l^j f_L(l)dl = j!\tau^j \int_0^{\infty} g^j f_G(g)dg \tag{10}$$

The left hand side of Eq. 10 is the $j$th moment about the origin of the CSD, and the integral on the right hand side is the $j$th moment about the origin of the growth rate distribution. Thus,

$$m_L(j) = j!\ \tau^j m_G(j) \tag{11}$$

For $j = 1$ and $j = 2$,

$$m_L(1) = \tau m_G(1) \tag{12}$$

and

$$m_L(2) = 2\tau^2 m_G(2) \tag{13}$$

From Eqs. 12 and 13, the coefficient of variation of the size distribution can be related to the coefficient of variation of the growth rate distribution by

$$CV_L = \sqrt{2CV_G^2 + 1} \tag{14}$$

To demonstrate the use of Eq. 11, the CSD function $f_L(l)$ was generated by integrating Eq. 9 for a known growth rate distribution. The gamma distribution, which is given by Eq. 15, was used.

$$f_G(g) = \frac{1}{\beta^\alpha \Gamma(\alpha)} g^{\alpha-1} \exp(-g/\beta) \quad g > 0, \quad \alpha > 0, \quad \beta > 0 \tag{15}$$

The moments of the gamma distribution are given by

TABLE 1. COMPARISON BETWEEN THEORETICAL AND CALCULATED MOMENTS OF GROWTH RATE DISTRIBUTION

Growth rate distribution: Gamma

Form: $f_G(g) = \frac{1}{\beta^\alpha \Gamma(\alpha)} g^{\alpha-1} \exp(-g/\beta)$

$\bar{g} = 0.2, \quad CV = 0.5$

Parameters: $\alpha = 4, \quad \beta = 0.5, \quad \tau = 5.0$

| Order of the moment, $j$ | $m_L(j)$ | $j!$ | $\tau^j$ | $\frac{m_G(j)}{j!\tau^j}$ Calculated* $\frac{m_L(j)}{j!\tau^j}$ | $\frac{m_G(j)}{j!\tau^j}$ Theoretical** $\frac{\beta^j\Gamma(\alpha+j)}{\Gamma(\alpha)}$ |
|---|---|---|---|---|---|
| 0 | 1.007 | 1 | 1 | 1.0070 | 1.0 |
| 1 | 0.995 | 1 | 5 | 0.190 | 0.20 |
| 2 | 2.494 | 2 | 25 | 0.0499 | 0.05 |
| 3 | 11.04 | 6 | 125 | 0.0147 | 0.015 |
| 4 | 73.68 | 24 | 625 | 0.00491 | 0.00525 |
| 5 | 659.57 | 120 | 3125 | 0.00176 | 0.00210 |

* From Eq. 11.
** From Eq. 16.

$$m_G(j) = \beta^j \Gamma(\alpha + j)/\Gamma(\alpha) \tag{16}$$

The moments of the growth rate distribution were calculated using Eq. 11 with the CSD obtained from Eq. 9. These calculated moments were compared to the moments calculated from Eq. 16 which we refer to as theoretical moments. The comparison is shown in Table 1. For the computer generated CSDs, the difference between actual and theoretical moments becomes larger when considering the fourth moment and above. This is most likely due to the truncation involved in calculating the moments from the CSD. For the idealized distributions, the size is allowed to vary from 0 to $\infty$. Truncating the size range over which the integration to calculate $m_L(j)$ is used leads to a slight error. This is true because even though the population density is small, at the large sizes the weighting factor (e.g., $L^4$ for the fourth moment) becomes very large. This should be less of a problem with real distributions since the size does have some physical upper limit.

The first and second moments of the growth rate distribution can be computed from the CSD with accuracy as is shown in Table 1. Thus, it appears that from actual experimental data, the mean and variance of the growth rate distribution can be obtained from the CSD from an MSMPR crystallizer.

### Inverse Gamma Growth Distribution

It is interesting to consider a growth rate distribution which has an explicit solution from the preceding analysis. Janse and deJong (1976) proposed a distribution resembling a distribution obtained by substituting the reciprocal of the random variable instead of the random variable in the gamma probability density function. For the sake of convenience this is called the inverse gamma distribution; it is given below:

$$f_G(g) = \frac{a^{k-1}}{\Gamma(k-1)} g^{-k} \exp(-a/g) \quad a > 0, \quad k \geq 3 \tag{17}$$

The properties of inverse gamma GRD are listed in Table 2.

Substituting Eq. 17 in Eq. 9 and integrating yields

$$f_L(l) = (k-1)(a\tau)^{k-1}/(l + a\tau)^k \tag{18}$$

Or in terms of the mean growth rate $\bar{g}$ and the parameter $k$,

$$f_L(l) = (k-1)[(k-2)\bar{g}\tau]^{k-1}/[l + (k-2)\bar{g}\tau]^k \tag{19}$$

For no growth rate dispersion, $(CV_G) = 0$, which occurs when $k \to \infty$,

$$f_L(l)|_{k\to\infty} = 1/\bar{g}\tau \exp(-l/\bar{g}\tau) \tag{20}$$

which is the equation for an ideal MSMPR without growth rate dispersion.

TABLE 2. PROPERTIES OF INVERSE GAMMA GROWTH RATE DISTRIBUTION

Form: $f_G(g) = \frac{a^{k-1}}{\Gamma(k-1)} g^{-k} \exp(-a/g) \quad a > 0, \quad k \geq 3$

1. $\int_0^\infty f_G(g)dg = 1$
2. $f_G(g = 0) = 0$
3. Mean, $\bar{g} = \frac{a}{k-2}$
4. Variance, $\sigma_G^2 = \frac{a^2}{(k-2)^2(k-3)}$
5. $CV_G = \sqrt{\frac{1}{k-3}}$
6. The $j$th moment about the origin is

$$M_G(j) = a^j \frac{\Gamma(k-1-j)}{\Gamma(k-1)} \text{ for } j < k-1$$

The properties of the CSD for the specific case when GRD is the inverse gamma are given in Table 3.

The first four moments of the CSD (assuming a constant shape factor of unity) about the origin are

$$m_L(0) = 1 \tag{21}$$

$$m_L(1) = \bar{g}\tau \tag{22}$$

$$m_L(2) = 2(\bar{g}\tau)^2(k-2)/(k-3) \tag{23}$$

$$m_L(3) = 6(\bar{g}\tau)^3(k-2)^2/(k-3)(k-4) \tag{24}$$

The number, length and area mean sizes, respectively, are

$$\bar{L}_{1,0} = \bar{g}\tau \tag{25}$$

$$\bar{L}_{2,1} = 2\bar{g}\tau(k-2)/(k-3) \tag{26}$$

$$\bar{L}_{3,2} = 3\bar{g}\tau(k-2)/(k-4) \tag{27}$$

The dominant crystal size, the mode of the area distribution, is

$$\bar{L}_D = 3\bar{g}\tau(k-2)/(k-4) \tag{28}$$

and the coefficient of variation of the mass distribution is

$$CV_M = \tfrac{1}{2}\sqrt{(k-1)/(k-6)} \tag{29}$$

Thus, when the growth rate distribution can be described by an uncommon distribution such as the inverse gamma distribution,

TABLE 3. PROPERTIES OF CRYSTAL SIZE DISTRIBUTION FROM MSMPR CRYSTALLIZER FOR INVERSE GAMMA GROWTH RATE DISTRIBUTION

Form: $f_L(l) = \frac{(k-1)(a\tau)^{k-1}}{(l + a\tau)^k}$

1. $\int_0^\infty f_L(l)dl = 1$
2. $f_L(l = 0) = \frac{(k-1)}{(k-2)\bar{g}\tau}$
3. Mean size, $\bar{l} = \bar{g}\tau$
4. Variance, $\sigma_L^2 = (\bar{g}\tau)^2 \frac{(k-1)}{(k-3)}$
5. $CV_L = \sqrt{\frac{k-1}{k-3}}$
6. The $j$th moment of the CSD about the origin is

$$M_L(j) = (k-1)(k-2)^j(\bar{g}\tau)^j \frac{\Gamma(j+1)\Gamma(k-(j+1))}{\Gamma(k)}$$

for $j < k-1$

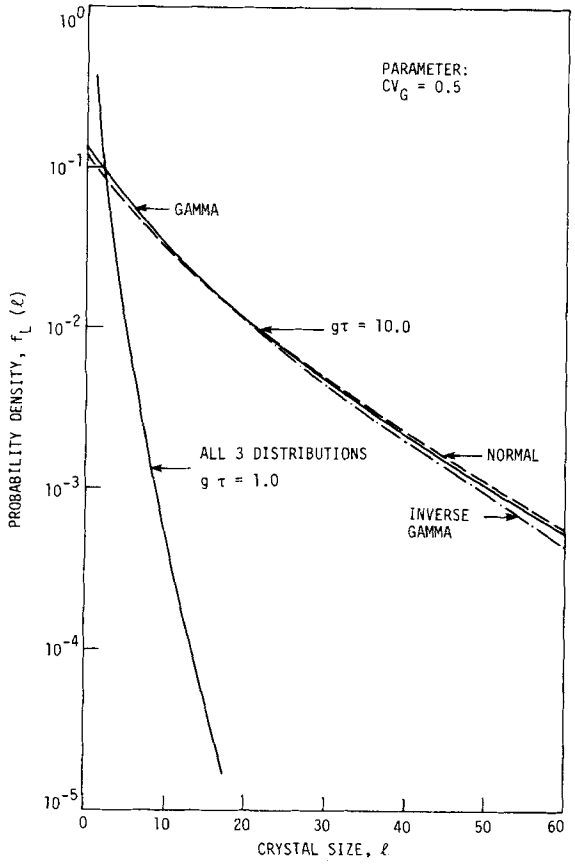


**Figure 1. Comparison between probability densities $f_L(l)$ for different growth rate distributions with the same $CV_G$ and various $\bar{g}\tau$.**

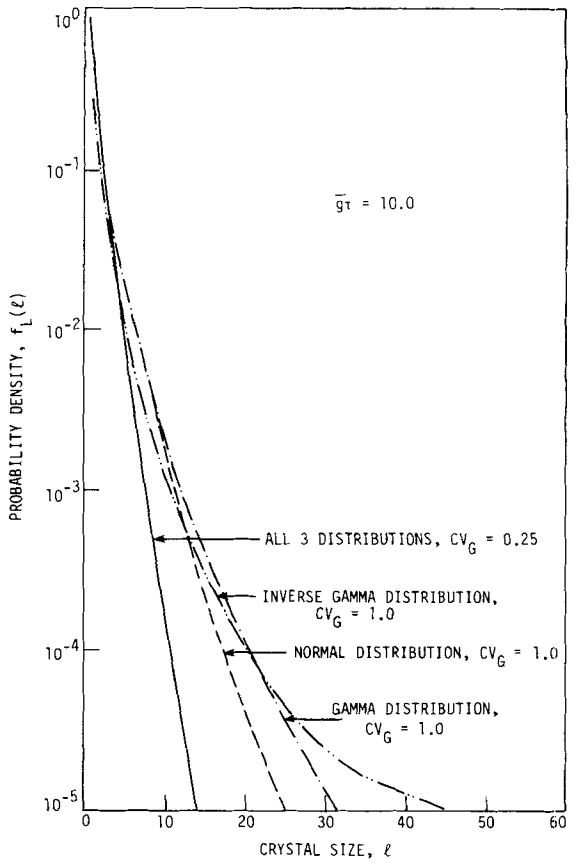


**Figure 2. Comparison between probability densities $f_L(l)$ for different growth distributions with various $CV_G$ and constant $\bar{g}\tau$.**

it is possible to characterize the CSD from an MSMPR crystallizer by an explicit analytical equation, along with all of its properties such as mean size, $CV_L$, etc.

### Effect of the Nature of the Distributions on CSD

In order to study the effect of the various growth rate distributions on CSD, three different distributions with the same $CV_G$ and mean growth rate, $\bar{g}$, were used. The distributions considered were

1. Gamma distribution.
2. Normal distribution.
3. Inverse Gamma distribution.

Since these growth distributions are two-parameter models, by specifying the $CV_G$ and the mean it is possible to express the parameters in terms of $CV_G$ and the mean. Further, for the sake of simplicity and comparison, the growth rate was made dimensionless by $x = g/\bar{g}$. Thus, for the above mentioned growth rate distributions, the corresponding CSDs from Eq. 9 with $CV_G$ and $\bar{g}\tau$ as parameters are

*Gamma GRD:*

$$f_L(l) = c_1 \int_0^\infty \frac{1}{\bar{g}\tau x} \exp\left\{-\frac{l}{\bar{g}\tau x} - \frac{x}{(CV_G)^2}\right\} x^{c_2} dx \qquad (30)$$

where

$$c_1 = [(CV_G^2)^{1/CV_G^2}\Gamma(1/CV_G^2)]^{-1} \qquad (31)$$

$$c_2 = (1 - (CV_G)^2)/(CV_G)^2 \qquad (32)$$

*Normal GRD:*

$$f_L(l) = c_3 \int_0^\infty \frac{1}{\bar{g}\tau x} \exp\left\{-\frac{l}{\bar{g}\tau x} - \frac{1}{2}\left(\frac{x-1}{CV_G}\right)^2\right\} dx \qquad (33)$$

$$c_3 = (1/(CV_G))/\sqrt{2\pi} \qquad (34)$$

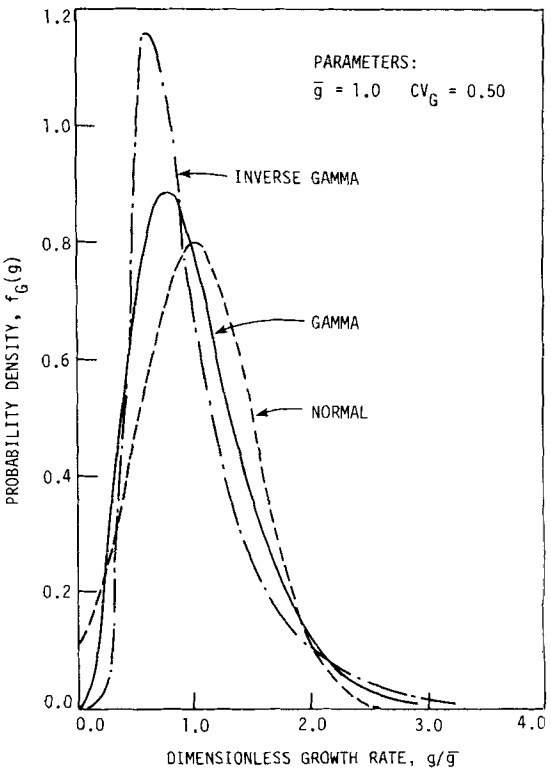


**Figure 3. Growth rate distributions for $CV_G$ = 0.5 and $\bar{g}$ = 1.0.**

*Inverse Gamma GRD:*

$$f_L(l) = \frac{c_4}{\bar{g}\tau}\left\{1 + \frac{(CV_G)^2}{\bar{g}\tau[(CV_G)^2 + 1]}\right\}^{-c_5} \quad (35)$$

$$c_4 = \frac{2(CV_G)^2 + 1}{(CV_G)^2 + 1} \quad (36)$$

$$c_5 = \frac{3(CV_G)^2 + 1}{(CV_G)^2} \quad (37)$$

CSD's were generated for all three distributions for different values of $CV_G$ *and* $\bar{g}$; these are plotted in Figures 1 and 2. It can be seen from Figures 1 and 2 that for values of $CV_G$ less than 0.5, there is very little difference in the population densities. Even at a $CV_G$ value of 1.0, the difference in $f_L(l)$ values between the three different distributions is not substantial. Also, for the sake of illustration, growth rate distributions for typical values of $CV_G$ and $\bar{g}$ are shown in Figure 3.

## CONCLUSIONS

The analysis presented allows the calculation of the variance and mean of the growth rate distribution from the CSD of an MSMPR crystallizer. This is true for the case when the CCG model presented by Berglund and Larson (1984) is applicable. Three different distributions for the growth rate have been studied, and it appears that any reasonable distribution yields similar results for the CSD. Therefore, the variance and mean of the GRD are recoverable from the CSD.


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## NOTATION

$a$ = parameter for the inverse gamma growth rate distribution, m/h
$B^0$ = nucleation rate, ("number")/m$^3$·h
$CV_X$ = coefficient of variation for the random variable $x$
$f_X(x)$ = probability density function for the random variable $x$/$x$·m$^3$
$F_X(x)$ = cumulative distribution function for the random variable $x$/m$^3$
$g$ = individual linear growth rate, m/h
$\bar{g}$ = mean linear growth rate, m/h
$k$ = parameter for the inverse gamma growth rate distribution
$l$ = individual crystal size, m
$L_D$ = dominant crystal size, m
$L_{p+1,p}$ = weighted mean size of the CSD, $m_L(p + 1)/m_L(p)$, m
$m_x(j)$ = $j$th moment of the probability density function, $f_X(x)$, about the origin
$n$ = number density of crystals/m·m$^3$
$n^0$ = number density of nuclei/m·m$^3$
$x$ = dimensionless growth rate

### Greek Letters

$\Gamma(x)$ = gamma function
$\tau$ = mean holding time, h

### Subscripts

$G$ = growth rate distribution
$L$ = crystal size distribution
$M$ = mass distribution

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