Initial Condition for Population Balance in an MSMPR Crystallizer

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Secondary contact nuclei are born in a wide range of sizes (Garside et al., 1979). The process can be called size distributed nucleation. Semilogarithmic population density plots of a crystal product from MSMPR (mixed-suspension, mixed-product-removal) crystallizers frequently show concave-upward curvature. This has been explained either by the apparent size-dependent growth of crystals or by the phenomenon of crystal growth rate dispersion. Even though most of recent experiments support the latter reason, experimental data from MSMPR crystallizers still are considered to yield kinetics under the assumption of size-dependent growth, partly because it is just easier.

When size distributed nucleation, size-dependent growth, and negligible crystal attrition are assumed, the population balance in an MSMPR crystallizer at a steady state is

$$b(L)dL - d[G(L)n(L)] = \frac{n(L)}{\tau}dL \tag{1}$$

The terms in the left side are input number rate by nuclei birth and net input of crystals by growth, respectively. The right side term represents output of crystals in the product suspension.

The partial-differential form of Eq. 1 was used by Youngquist and Randolph (1972). Randolph and Cise (1972). Randolph and Sikdar (1976) in their attempts to estimate two unknown functions, $b(L)$ and $G(L)$, from experimental $n(L)$ data. Briefly, the basis of the procedure used by them for estimation of the total nucleation rate, B_T, via birth function, $b(L)$, was the following. Smaller sizes are mostly populated by birth because the growth rate of small crystals is very low. Thus it was assumed that

$$\frac{d}{dL}[G(0)n(0)] \equiv G(0)\frac{dn(0)}{dL} + n(0)\frac{dG(0)}{dL} \simeq 0 \tag{2}$$

Substituting Eq. 2 to Eq. 1 gave the following approximation:

$$b(L) \simeq n(L)/\tau \tag{3}$$

believed to be valid in the small size range with accuracy decreasing with size. The total nucleation rate was then estimated from the equation

$$B_T \equiv \int_0^\infty b(L)\,dL \simeq \frac{1}{\tau}\int_0^\infty n(L)\,dL \tag{4}$$

where the upper limits of integration were, in fact, a finite numbers.

It is shown that simplifying assumption 2 and its result (Eq. 3) is both erroneous and unnecessary to obtain Eq. 4, which is generally and strictly valid for some other reason. The proper initial condition for balance (Eq.) is derived and its consequences are discussed.

Initial Condition

Randolph and his coworkers (1972, 1976) did not attempt to derive the initial condition for Eq. 1 prior to any speculations. Let's do it, assuming the following for generality:

- The smallest size of nuclei is $L_n \geq 0$.
- The growth and birth functions are finite and known. The last one can be of any form except for the Dirac delta function $\delta(L)$. The second left-side term in Eq. 1 the net flux by growth equals

$$d(Gn) \equiv G(L + dL)n(L + dL) - G(L)n(L) \tag{5}$$

It is physically evident that, for the size exactly L_n there is no gross crystal input caused by growth, since the smallest nuclei are of size L_n and the growth process itself does not populate it. Rather, there is the substantial gross output by growth as represented by the first right-side term of Eq. 5. Thus one can guess intuitively that the product $G(L_n)n(L_n)$ must equal zero. This would be the proper initial condition needed to solve Eq. 1 which can formally be proved as follows.

To conserve the number of particles in the whole size range (L_n, ∞), the total rate of nuclei birth in an MSMPR crystallizer must equal the total number of product crystals leaving it in a unit of time, that is

$$VB_T = qN_T \quad \text{or} \quad B_T = N_T/\tau \tag{6}$$

where the total nucleation rate is

$$B_T = \int_{L_n}^{\infty} b(L)\, dL \tag{7}$$

and the total number of crystals in a suspension volume unit is

$$N_T = \int_{L_n}^{\infty} n(L)\, dL \tag{8}$$

The absolute equality (Eq. 6) is thus identical to the supposed approximation (Eq. 4) and rigorous in general.

Integrating Eq. 1 in the whole size range gives

$$\int_{L_n}^{\infty} b(L)\, dL - G(\infty)n(\infty) + G(L_n)n(L_n) = \int_{L_n}^{\infty} \frac{1}{\tau} n(L)\, dL \tag{9}$$

The product $G(\infty)n(\infty)$ must equal zero as the probability of reaching infinite size for a crystal is zero, that is

$$\lim_{L \to \infty} n(L) = 0 \tag{10}$$

It should be evident again that also the product $G(L_n)n(L_n)$ must equal zero, since there is no flux of crystals to size L_n caused by growth. If it were, one would obtain the contradiction to Eq. 6, namely

$$B_T + G(L_n)n(L_n) \neq N_T/\tau \tag{11}$$

unless $G(L_n) = 0$, which is unrealistic. Thus the following indentity must hold

$$G(L_n)n(L_n) \equiv 0 \tag{12}$$

Equation 12 is the proper initial condition for balance (Eq. 1). It is universal as it includes specific cases such as:

$$b(L_n) = 0,$$

$$G(L_n) = 0,$$

$$G = \text{const.}$$

Discussion

Let us consider some implications of initial condition (Eq. 12). If $G(L_n) > 0$, the population density of crystals at the minimum size must equal

$$n(L_n) \equiv 0 \tag{13}$$

It equals zero even if $b(L_n) > 0$ which seems to be doubtful at first sight. It is instructive to replace the birth function by a more physically obvious concept of population density of nuclei at the moment of their birth, $n_n(L)$. Both functions are not measurable directly. They are interrelated

$$Vb(L) = qn_n(L) \quad \text{or} \quad b(L) = n_n(L)/\tau \tag{14}$$

Equation 14 is similar to Eq. 3, but it contains population density of nuclei and not of crystals. Substituting Eq. 14 to Eq. 1 gives the alternative form of the population balance

$$n_n(L)/\tau - \frac{d}{dL}[G(L)n(L)] = n(L)/\tau \tag{15}$$

As a rule, $n_n(L)$ decreases and $G(L)$ increases with size. The question arises: why population density of *crystals* $n(L)$ at size L_n is zero even if population density of *nuclei* $n_n(L_n)$ is greater than zero? It is so because the growth term $d(Gn)/dL$ at the point $L = L_n$ equals exactly $n_n(L_n)/\tau$. Thus the term is positive and represents the net output by growth from size L_n. With increasing size the term decreases to zero, and both functions, $n(L)$ and $n_n(L)$, become equal for the only size L_d which corresponds to the maximum of $n(L)$. The term becomes negative for larger sizes: that is, it actually represents the net input. As the second input term $n_n(L)/\tau$ is negligible, the former causes $n(L)$ function to decrease with size.

Equation 15 shows that the forcing function $n_n(L)$ is a different quantity than the resulting $n(L)$ function. Randolph and Larson (1988) interchangeably used both of the terms "population density of nuclei" and "population density of the nucleus-size crystals" for n^o. It is confusing in light of the fact that the first term corresponds to the infinite value for monosized nuclei while the second, to the finite value concerning crystals.

Substituting $L = L_n$ and Eq. 13 to balance (Eq. 1) gives

$$b(L_n) = \frac{d}{dL}[G(L_n)n(L_n)] > 0 \tag{16}$$

Compare Eqs. 16 and 2. It is the derivative which determines the value of birth function in the close proximity of size L_n but not the very low population density as suggested incorrectly by Eq. 3. Approximation (Eq. 2) and its result (Eq. 3) are merely valid but strictly for the particles (nuclei and crystals) which do not grow at all. Then differential population balance (Eq. 1) is reduced to the algebraic form of Eq. 3, that is

$$b^*(L) = n^*(L)/\tau \tag{17}$$

The superscript (*) denotes nongrowing particles. When both growing and nongrowing particles are present in a crystallizer, one needs two separate number balance equations, i.e., Eqs. 1 and 17. The population density function $n_p(L)$ of product crystals is then the sum of $n(L)$ and $n^*(L)$.

Both definite integrals in Eq. 9 are only equal because crystal flux by growth is zero at both ends of the size range L_n, ∞. The integrands, however, do not equal each other by any means! This can be demonstrated by solving Eq. 1 with condition (Eq. 13) and with simplifying assumptions: $G(L) = \text{const}$, $L_n = 0$, the exponential form of the birth function (nuclei size distribution)

$$b(L) = B_T \exp(-L/\bar{L}_n)/\bar{L}_n = n_n(L)/\tau \tag{18}$$

The solution is

$$n(L) = \frac{B_T \tau}{G\tau - \overline{L}_n} \left(\exp\left[-\frac{L}{G\tau} \right] - \exp\left[-\frac{L}{\overline{L}_n} \right] \right) \qquad (19)$$

Comparison of Eqs. 18 and 19 shows that the first function decreases steadily while the second one undergoes a maximum.

Size distributed birth of contact nuclei has convincingly been proved by experiments. However, nobody observed a maximum on any population density plot down to the size of 1 μm. That probably occurs at some smaller size, unmeasurable as yet.

The population balance for the case of size distributed nucleation and permanent growth dispersion [called Constant Crystal Growth by Larson at al. (1985)] is similar to Eq. 1, but is formulated in terms of two-dimensional, modified population density function $f(L,G)$ (see Janse and de Jong, 1976). The maximum on the population density plot was found also for the case by Berglund and Larson (1984) in their modeling studies. They attribute this solely to the assumed boundary value of nuclei size distribution ($n_n(L_n) = 0$ [$\lambda(L_i = 0) = 0$ in their notation]. By analogy of their two-dimensional case with the one-dimensional case considered the maximum should also appear when $n_n(L_n) > 0$.

Notation

B_T = total nucleation rate, $1/m^3 \cdot s$
$b(L)$ = birth function of nuclei, $1/m^4 \cdot s$
$G(L)$ = size-dependent growth rate, m/s
L_n = minimum size of nuclei, m
$\overline{L}_n$ = mean size of nuclei, m
N_T = total number of crystals in m^3 of suspension
$n(L)$ = population density of crystals, $1/m^4$
$n_n(L)$ = population density of nuclei at birth, $1/m^4$
q = volumetric flow rate of suspension, m^3/s
V = crystallizer volume, m^3
τ = mean residence time, s

Literature Cited

Berglund, K. A., and M. A. Larson, "Modeling of Growth Rate Dispersion of Citric Acid Monohydrate in Continuous Crystallizers," *AIChE J.*, **24**(2), 280 (1984).

Garside J., I. T. Rusli, and M. A. Larson, "Origin and Size Distribution of Secondary Nuclei," *AIChE J.*, **25**(1), 57 (1979).

Janse, A. H., and E. J. de Jong, "The Occurrence of Growth Dispersion and its Consequences," *Industrial Crystallization*, J. W. Mullin, ed., p. 145 Plenum Press, New York (1976).

Larson, M. A., E. T. White, K. A. Ramanarayanan, and K. A. Berglund, "Growth Rate Dispersion in MSMPR Crystallizers," *AIChE J.*, **31**(1), 90 (1985).

Randolph, A. D., and M. D. Cise, "Nucleation Kinetics of the Potassium Sulfate—Water Systems," *AIChE J.*, **18**(4), 798 (1972).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*. pp. 86, 107 Academic Press, New York (1988).

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

Youngquist, G. R., and A. D. Randolph, "Secondary Nucleation in a Class II System: Ammonium Sulfate-Water," *AIChE J.*, **18**(2), 421 (1972).

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