CRYSTALLIZATION IN A CASCADE OF IDEALLY STIRRED VESSELS. ANALYTICAL DESCRIPTION OF MOMENTS OF THE DISTRIBUTION FUNCTION OF PARTICLE SIZES OF THE CRYSTALLINE SUSPENSION

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The calculation method of moments of particle size distribution function is demonstrated on the cascade of ideally stirred vessels in which the growth and dissolving of crystals takes place alternately. Advantage of this method lies in the possible direct evaluation of moments without the need to determine and integrate the function itself.

The particle size distribution is of primary importance in studies on the phenomena concerning the system of particles of various sizes (especially in description of the treatment of crystalline suspensions). It is often advantageous to express the properties of distribution functions by use of their global characteristics. Among the most important characteristics belong the first general moments. The mathematical model of an operation with a system of particles is significantly simplified as far as the knowledge of moments of the corresponding distribution function suffices for the description of the phenomena and as long as one succeeds to make the description so that these moments are evaluated directly and not on basis of the knowledge of the distribution function itself. For the simple example of the cascade of ideally stirred crystallizers the description containing this advantageous property is derived.

THEORETICAL

Let us consider a cascade of ideally stirred vessels having the same volume V, which are being kept at the same temperature T_1 (all odd vessels of the cascade) and T_2 (all even), $T_1 < T_2$. The solution is fed into the first vessel at the temperature T_s, $T_1 < T_s < T_2$, so that in odd members of the cascade the crystals grow at the rate v_i while in even members the dissolving takes place.

The balance of normalized probability densities $y(r)$ of the occurence of particles of the size r in the i-th member of the cascade in the dimensionless form is given by the relation

$$a_i y_{i-1} + (-1)^i \, dy/dr - a_i y_i = 0 \,, \tag{1}$$

where $a_i = w/(V|v_i|)$, and w is the volumetric flow rate of the inlet and outlet streams. The boundary conditions are derived from the integral shape of the equation (1)

$$a_i \int_0^\infty y_{i-1} \, dr - (-1)^i \, y_i(r = 0) - a_i \int_0^\infty y_i \, dr = 0 \,. \tag{2}$$

In those members of the cascade where the growth takes place the number of particles does not change, $\int_0^\infty y_{i-1} \, dr = \int_0^\infty y_i \, dr$, so that from Eq. (2) results

$$y_i(r = 0) = 0 \,, \quad i = 1, 3, 5, \ldots \,. \tag{3}$$

For the dissolving (even) members of the cascade can be derived (see Appendix I)

$$y_i(r = 0) = a_i \int_0^\infty y_{i-1} \exp(-ra_i) \, dr \,, \quad i = 2, 4, 6, \ldots \,. \tag{4}$$

If we take into consideration the well-known relation

$$\{y_{i-1} \exp(-a_i r)\} = \lim_{s \to 0} Y_{i-1}(s + a_i) \,,$$

where $\{y_i\} = Y_i$ is the Laplace transformation of the function y_i, the balance equations (1) together with the conditions (3) and (4) get the form after the Laplace transformation, for the i-th growth vessel

$$Y_i = [a_i/(s + a_i)] \, Y_{i-1} \,, \quad i = 1, 3, 5, \ldots \tag{5a}$$

and for the i-th dissolving vessel

$$Y_i = [-a_i/(s - a_i)] \, [Y_i - \lim_{s \to 0} Y_{i-1}(s + a_i)] \,, \quad i = 2, 4, 6, \ldots \,. \tag{5b}$$

By multiplication of Eq. (1) by the j-th exponent r and by the following integration the relations can be derived between the j-th moment in the i-th member of the cascade

$$M_j^i = \int_0^\infty r^j y_i \, dr \,,$$

and the moment of the lower order of the same member and of the same order of the preceeding member

$$M_j^i = M_j^{i-1} - (-1)^i (j/a_i) M_{j-1}^i . \tag{6}$$

For the zero moment holds

$$M_0^i = \int_0^\infty y_i \, dr = \lim_{s \to 0} Y_i . \tag{7}$$

TABLE I

Terms for Some First Moments M_j^i for the Case $Y_0 = 1$

i	$j = 0$
0	1
1	1
2	$a_2/(a_1 + a_2)$
3	$a_2/(a_1 + a_2)$
4	$M_0^2\{1 - a_1a_3/[(a_1 + a_4)(a_3 + a_4)]\}$
5	M_0^4
6	$M_0^4 - \dfrac{a_1a_2a_3a_4a_5(a_1 + a_3 + a_4 + a_6)/(a_5 + a_6)}{(a_1 + a_2)(a_1 + a_4)(a_1 + a_6)(a_3 + a_4)(a_3 + a_6)}$
7	M_0^6
8	$M_0^6 - [a_1a_2a_3a_4a_5a_6a_7(2a_1 + 2a_3 + 3a_4 - a_5)]/ /[(a_1 + a_2)(a_1 + a_4)(a_1 + a_6)(a_1 + a_8)(a_3 + a_4)(a_3 + a_8)(a_3 + a_6)(a_5 + a_6)(a_5 + a_8)(a_7 + a_8)]$
9	M_0^8

i	$j = 1$	$j = 2$	$j = 3$
0	0	0	0
1	$1/a_1$	$2/a_1^2$	$6/a_1^3$
2	$\dfrac{1}{a_1} - \dfrac{1}{a_1 + a_2}$;	$2\left[\dfrac{1}{a_1^2} - \dfrac{1}{a_1a_2} - \dfrac{1}{a_2(a_1 + a_2)}\right]$;	$6\left[\dfrac{1}{a_1^3} - \dfrac{1}{a_2}\left(\dfrac{1}{a_1^2} - \dfrac{1}{a_1a_2} - \dfrac{1}{a_2(a_1 + a_2)}\right)\right]$;
3	$\dfrac{1}{a_1} - \dfrac{1}{a_1 + a_2}\left(\dfrac{a_2}{a_3} = 1\right)$;	$2\left[\dfrac{1}{a_1^2} - \dfrac{1}{a_1a_2} + \dfrac{1}{a_1a_3} - \dfrac{1 + a_3 - a_2}{a_1 + a_2}\right]$;	$M_3^2 + \dfrac{3}{a_3} M_2^3$
4	$M_1^3 - \dfrac{1}{a_4} M_0^4$	$M_2^3 - \dfrac{2}{a_4} M_1^4$	$M_3^4 = M_3^2 - \dfrac{3}{a_4} M_2^4$

From Eqs (2) and (3) or from Eq. (5a) results for the odd members $M_0^i = M_0^{i-1}$, $i = 1, 3, 5, \ldots$. Let us now consider the inlet distribution of particles y_0 described by the Dirac function δ; then $Y_0 = 1$, and from relations (5) to (7) the individual moments result as functions of parameters a_i, see Table I.

If in the unit of volume of the first crystallizer originates in a unit of time $\tau(\tau = tV/w)$ $\dot{n}$ particles, then in the unit of volume of the outlet stream is n particles, $n = \dot{n}V/w$. The number of particles leaving the i-th vessel is wnM_0^i. The material balance for the first vessel is

$$wc_0 = wc_1 + wn\xi M_3^1 , \qquad (8)$$

where ξ is the shape and volume factor. Similarly it holds for the i-th member

$$c_{i-1} - c_i = (-1)^{i+1} n\xi(M_3^i - M_3^{i-1}) = (-1)^{i+1} 3n\xi M_2^i/a_i . \qquad (9)$$

From Eq. (6) results for M_2^i

$$M_2^i = M_2^{i-1} + (-1)^{i+1} \frac{2}{a_i} \sum_{n=1}^{i} (-1)^{n+1} \frac{M_0^n}{a_n} .$$

Let us denote the equilibrium concentrations at temperatures T_1 and T_2, $c_1^* = c^*$, $c_2^* = c^* + \Delta$ and let us assume that the growth rate and dissolving of particles is described by relations

$$\dot{r} = dr/d\tau_{T_1} = k(c - c_1^*) , \quad -dr/d\tau_{T_2} = k(c_2^* - c) ,$$

then for a_i holds

$$a_i = q/(c_i - c^*) \quad \text{for} \quad i = 1, 3, 5, \ldots \qquad (10a)$$

$$a_i = q/(c^* + \Delta - c_i) \quad \text{for} \quad i = 2, 4, 6, \ldots \qquad (10b)$$

where $q = w/(kV)$. Relations (9) and (10) represent $2m$ equations for $2m$ unknowns a_i, c_i, for m members of the cascade. By their common solution for the specified values of V, w, k, n, c^*, c_0, ξ, y_0, Δ the looked for values of M_j^i, a_i, c_i can be obtained for all members of the considered cascade (or the system of algebraic non-linear equations for a_i (see Appendix II) can be obtained by elimination of c_i from Eqs (9) and (10)).

RESULTS AND DISCUSSION

The studied operation represents the model of recrystallization of crystalline suspensions under the conditions of thermal oscilations. For recrystallization are typical the loss of a number of small crystals and the growth of larger crystals[1]. The zero moments should thus decrease with the increasing order number of the cascade member, and the third moments increase. We present for illustration the results (Table II) calculated by the presented procedure for typical values of inlet parameters taken from the monography by Mullin[2]: $V = 1\ dm^3$, $w = 0{\cdot}05\ dm^3/min$, $k = 10^{-5}\ dm^4/kg\ min$, $n = 10^6$ particles/dm^3 min, $c^* = 0{\cdot}110\ kg/dm^3$, $c_0 = 0{\cdot}120\ kg/dm^3$, $\Delta = 0{\cdot}020\ kg/dm^3$, $\xi = 1\ kg/dm^3$.

It is obvious that the resulting moments have the expected properties. It is interesting that the significant loss of particles takes place only in the first two or three dissolving crystallizers (value of the zero moment quickly converges to a certain limiting value with increasing i). Value of the first moment in the growth members of the cascade is almost constant. As can be seen from the relations given in Table I, it is the result of the fact that values a_i are in the chosen example very close (if the operation is carried out so that $a_1 = a_2 = a_3 \ldots$ this can be reached by a suitable selection of temperatures in each member of the cascade, where, of course, neither $T_1 \neq T_3 \neq T_5 \ldots$ nor $T_2 \neq T_4 \ldots$ – it can be then demonstrated that $M_1^1 = M_1^3 = M_1^5 \ldots$).

Equations from which the constants a_i were calculated (see Appendix II) have the so-called stiff character and are, therefore, very interesting from the point of view of numerical solution. This is the consequence of a wide range of the order of magnitude of values $\dot{r}$ ($\sim 10^{-8}$ m/s) and $\dot{n}$ ($\sim 10^{10}$ particles/m^3 s) in the given equations.

TABLE II

Calculated Moments of the Distribution Function of Crystal Sizes for the Model Case

i	M_0^i	$M_1^i \cdot 10^6$	$M_2^i \cdot 10^{12}$	$M_3^i \cdot 10^{17}$	$a_i - 5 \cdot 10^5$
0	1	0	0	0	—
1	1	2	8	4·8	0·48
2	0·5	1	4	2·4	−0·24
3	0·5	2	12	9·6	0·96
4	0·375	0·5	9	2·4	−0·54
5	0·375	2	21	19·2	1·56
6	0·3125	0·75	16	6·0	−0·63
7	0·3125	2	28	28·9	2·10
8	0·3125	0·75	24	9·6	−0·72
9	0·3125	2	36	28·4	2·64

This way for solution of practical examples arises the necessity to use computers for evaluation of numbers of more than 9 to 12 valid figures (*i.e.* to count with the doubled accuracy).

REFERENCES

1. Žáček S.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1976.
2. Mullin J. W.: *Crystallisation*, 2nd Ed. Butterworths, London 1972.

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APPENDIX I

From definition $-\mathrm{d}r/\mathrm{d}t = 1/a_i$, for the time f_i needed for the complete dissolving of the particle of the size r, results

$$f_i = -\int_r^0 a_i \, \mathrm{d}r = a_i r \, .$$

With regard to the assumption on ideal mixing in the i-th vessel, the probability density of residence of particle in the vessel is $\phi(t_i) = \exp(-t_i)$. The share of particles of the size r, which do not dissolve in the interval $\langle 0, f_i \rangle$ and leave the i-th vessel, is given by the relation $1\text{-}\exp(-f_i) = 1\text{-}\exp(-a_i r)$; the total number of particles which leave the i-th vessel is then given by the balance

$$\int_0^\infty y_i \, \mathrm{d}r = \int_0^\infty y_{i-1} \, \mathrm{d}r - \int_0^\infty y_{i-1} \exp(-a_i r) \, \mathrm{d}r \, .$$

By coupling this equation with the momentum equation (*2*) results the relation (*4*).

APPENDIX II

By coupling the relation (*9*) and (*10*), results a system of equations for a_i in the form

$$u_0 a_1^3 - q a_1^2 - 2s = 0 \, ,$$
$$a_2^2(\Delta - u_1) + a_2 a_1(\Delta - u_1) - q - 2s/a_1^2 - a_1 q = 0 \, ,$$
$$a_3^3 u_2 - a_3^2(q + sM_2^2) - 2sM_1^2 a_3 - 2sM_0^3 = 0 \, ,$$
$$a_i(\Delta - q/a_{i-1}) - sM_2^i - q = 0 \, , \quad \text{pro} \quad i = 4, 5, 6, \ldots \, ,$$

where $s = 3n\xi$, $u_i = c_i - c^*$ and where for M_2^i can be substituted the relations given in Table I.