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Modelling 2D Crystal Shape in Cooling Crystallization by Moment Method

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Abstract: Crystals produced in the process industry often exhibit anisotropic habits which can-not be described satisfactorily through one single characteristic size. Such crystals are formed because of the different growth rates of crystalline facets hence usually can be modeled as well defined geometrical bodies. The characteristic sizes of these facets are, in principle, internal properties of crystals and can be modeled by means of multidimensional population balance equations. Numerical solution of the multi-dimensional population balance equations, however, is a time consuming procedure so that applying the moment method, that has been very successful in 1D systems appears to be useful also in multidimensional cases.

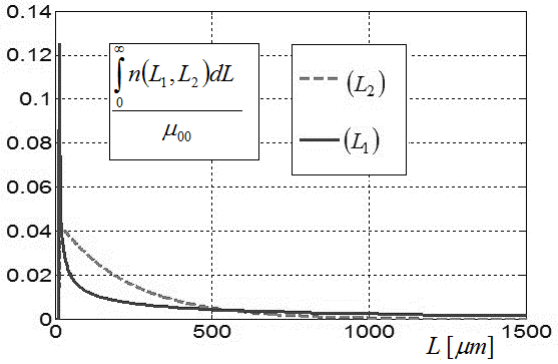
The aim of this work presents and discusses the moment method for characterizing the multidimensional population balance model describing crystallization from solution producing 2D habit crystals.

The initial step in this method is determining the 2D population balance model. We develop the population balance equation for 2D habit crystals describing the behavior of the population density function. Such crystals are characterized by two size dimensions *L1* and *L2*, while the crystal population is described by the population density function *n(.,.,t)*by means of which *n(L₁,L₂,t)* expresses the number of crystals from the size domain (*L₁,L₂+dL₁*)× (*L₁,L₂+dL₂*) in a unit volume of suspension at time t.

The moment equations in this case are formulated for joint moments where the joint (cross) moments are defined as:

$$\mu_{m_1,m_2}(t)=\int_0^\infty\int_0^\infty L_1^{m_1}L_2^{m_2}n(L_1,L_2,t)dL_1dL_2,\quad m_1,m_2=0,1,2,3,...$$

These moments determine some important properties of needle-shape or plate-like crystals, for example the number of crystal particles and crystal volume in solution. Therefore the model is suitable for computing the crystal size distribution which is very important property in industrial processes. For the sake illustration, the figures show the marginal size distribution functions of crystals obtained by the gamma distribution approximation:



The results obtained by simulation have revealed that the moment method can be used successfully for describe crystallization processes even in the case of 2D population balance models.

Keywords – Cooling crystallization, Population balance model, Moment method, joint moments

I. INTRODUCTION

Crystals produced by solution crystallization often exhibit anisotropic habits which cannot be described satisfactorily through one single characteristic size. Such crystals are formed because of different growth rates of crystalline facets and the characteristic sizes of these facets are, in principle, internal properties of crystals. In such cases crystallization processes are modeled by means of multidimensional population balance equations the numerical solution of which is a time consuming procedure. As a consequence, applying the moment method, that has proved very successful in treating 1D systems needs to be useful also in multidimensional cases.

2D population balance equations were solved by means of the quadrature method of moments (Wright et al, 2001; Marchisio and Fox, 2005), and this method was generalized also for multidimensional population balance models (Yoon and McGraw, 2004). Diemer and Olson (2006) applied the moment method with interpolation closure for analyzing aerosol reactors, Briesen (2006) developed a modified moment method for reducing a 2D population balance model of crystallization, and Lakatos (2008, 2010) and Borsos (2009) applied the cumulant-neglect closure method for closing 2D and 3D moment equations of joint moments in modeling micromixing in chemical reactors.

The aim of the work is to present and discuss the moment method applying the joint moments of characteristic edges of crystalline forms for describing crystallization from solution producing 2D habit crystals. A two dimensional model is developed for describing the evolution of needle-form crystals characterized by two size dimensions in cooling crystallization. Moment equation reductions for joint moments of internal variables are developed which, in the case of size independent growth are closed. The properties and behavior of the systems described by the models are investigated by simulation.

II. 2D POPULATION BALANCE MODEL: POPULATION BALANCE EQUATION

Crystalline particles often, especially in the pharmaceutical industry, exhibit needle-like habits, as it is illustrated in Figure1 with three different shapes. These needle-shape crystals are simple connected convex polyhedral which can be characterized by two size dimensions L_1 and L_2 which are sufficient to compute the volumes of crystals, required to develop the mass balance equation of solute. In this case the crystal population is described by the 2D population density function $(L_1, L_2, t) \to n(L_1, L_2, t)$ by means of which $n(L_1, L_2, t)dL_1 dL_2$ expresses the number of crystals from the size domain $(L_1, L_1 + dL_1) \times (L_2, L_2 + dL_2)$ in a unit volume of suspension at time *t*.

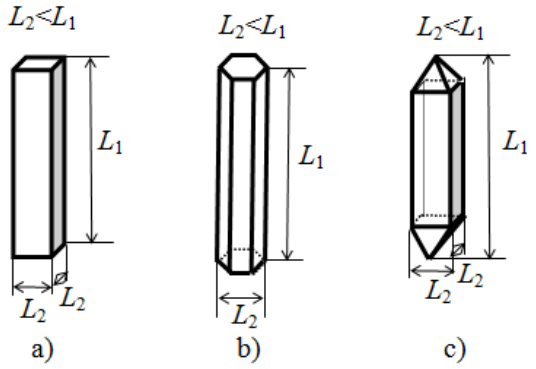


Figure 1. Three different two-dimensional crystal forms

Let us now assume that:

- The working volume of the crystallizer is constant;
- All new crystals are formed at a nominal size $L_{1,n} \cong L_{2,n} \cong L_{3,n} \cong L_n \geq 0$, so that we can assume: $L_n \approx 0$;
- Crystal breakage and agglomeration are negligible.

Under such conditions the population balance equation for crystals takes the form

$$\frac{\partial n}{\partial t} + \frac{\partial (G_1 n)}{\partial L_1} + \frac{\partial (G_2 n)}{\partial L_2} = \frac{1}{\tau}(n_{in} - n) + e_p B_p + e_b B_b \qquad (1)$$
$$0 < L_i < \infty,\ i = 1,2 \quad t > 0$$

subject to the appropriate initial and boundary conditions.

In Eq.(1), τ stand for the mean residence time, and e_p and e_b are binary existence variables by means of which the combination of the primary and secondary nucleation rates B_p and B_b, given by the Volmer and the power law models

$$B_p = k_p \varepsilon \exp\left(-\frac{k_e}{\ln^2\left(\frac{c}{c_s}\right)}\right) \qquad (2)$$

$$B_b = k_b (c - c_s)^b \mu_{1,2}^j \qquad (3)$$

can be controlled as $e_p + e_b \geq 1$. In Eq.(2) and Eq.(3), ε is the partial volume of solution in the suspension, expressed as

$$\varepsilon(t) = 1 - \iint_L \upsilon_c(L_1, L_2) n(L_1, L_2, t) dL_1 dL_2 \qquad (4)$$

and u_c is the volume of a single crystal depending on sizes L_1 and L_2.

The overall linear growth rates of the two habit faces, G_1 and G_2 are assumed to be size independent and have the forms of power law expressions

$$G_1 = k_{g_1}(c - c_s)^{g_1} \text{ and } G_2 = k_{g_2}(c - c_s)^{g_2} \quad (5)$$

In Eq.(2)-(5), c and c_s denote, respectively, the solute and equilibrium saturation concentrations while the kinetic coefficients *kg1*, *kg2*, *kp* and *kb* are functions of the temperature.

III. 2D POPULATION BALANCE MODEL: MOMENT EQUATION

In order to develop the mass and heat balance equations for the crystallizer requires an expression for the total mass of crystals. It has to be expressed by means of the volume of a single crystal, as given in Eq.(3), computed by means of the two identified sizes L_1 and L_2 of crystals. For instance, in the case of form by Fig.1a, the volume of a single crystal is expressed as

$$\upsilon_c(t) = L_1 L_2^2 \quad (6)$$

hence the partial volume of crystals in the suspension is given as

$$1 - \varepsilon(t) = \iint_L L_1 L_2^2 n(L_1, L_2, t) dL_1 dL_2 = \mu_{1,2} \quad (7)$$

Therefore, the partial volume of crystals in the suspension, required writing the mass balance, and also the heat balance equations can be expressed by means of the joint moment $\mu_{1,2}$ of crystal sizes L_1 and L_2. As a consequence, the mass balance of solute takes the form

$$\frac{dc}{dt} = \frac{\varepsilon_{in}}{\tau\varepsilon}(c_{in} - c) - \frac{\rho - c}{\varepsilon}\frac{d\mu_{1,2}}{dt} \quad (8)$$

so that variation of the first derivative of moment $\mu_{1,2}$ has to be tracking during the course of the process. This can be done by solving the population balance Eq.(1) using some numerical method, or by developing a set of moment equations for the joint moments

$$\mu_{k,m}(t) = \int_0^\infty \int_0^\infty L_1^k L_2^m n(L_1, L_2, t) dL_1 dL_2 \quad (9)$$

$$k, m = 0,1,2...$$

required computing the first derivative of moment $\mu_{1,2}$ directly. The second, i.e. moment method usually means much simpler and shorter computations although it provides only an approximation for the population density function from the joint moments.

In this 2D case, the infinite hierarchy of the moment equations corresponding to Eq.(1) takes the form

$$\frac{d\mu_{0,0}}{dt} = \frac{1}{\tau}(\mu_{0,0,in} - \mu_{0,0}) + e_p B_p + e_b B_b \quad (10)$$

$$\frac{d\mu_{k,m}}{dt} = \frac{1}{\tau}(\mu_{k,m,in} - \mu_{k,m}) + kG_1\mu_{k-1,m} + mG_2\mu_{k,m-1} \quad (11)$$

$$k, m = 1,2,3...$$

from which a finite closed set of equations, written for the moments $\mu_{0,0}, \mu_{1,0}, \mu_{0,1}$, $\mu_{0,2}, \mu_{2,0}$ and $\mu_{1,1}$ is required to compute the volume moment $\mu_{1,2}$ directly.

As a consequence, the complete moment equation model of the crystallizer consists of these moment equations as well as of the differential equations written for concentrations of solute and solvent, and for temperatures of the crystalline suspension and cooling medium. As an illustrative example, the differential equation describing variation of the solute concentration takes the form

$$\frac{dc}{dt} = \frac{\varepsilon_{in}}{\tau\varepsilon}(c_{in} - c) + \frac{\rho - c}{\varepsilon}\left[k_{g_1}(c - c_s)^{g_1}\mu_{0,2} + k_{g_2}(c - c_s)^{g_2}\mu_{1,1}\right] \quad (12)$$

i.e. the $\mu_{0,2}$ and $\mu_{1,1}$ moments are needed to close that that form.

IV. SIMULATION RESULTS AND DISCUSSION

The system of 11 ordinary differential equations describing the time evolution of variables $\mu_{0,0}, \mu_{1,0}, \mu_{0,1}, \mu_{0,2}, \mu_{2,0}, \mu_{1,1}, \mu_{1,2}$, c, c_{sv}, T, T_h was solved in Matlab environment. The basic values of kinetic parameters of nucleation and crystal

growth used in simulation are listed in the Table 1.

Table 1. Basic kinetic and process parameters used in simulation

k_p=1,6·10^{30} [m-3 s-1]	k_{g1}=12.2·10^{-6} [m s-1]
k_e=1.0	k_{g2}=10.08·10^{-7} [m s-1]
k_b=1.0·10^{16} [m-3-j s-1]	g_1=1.5
b=3.0 j=1.5	g_2=1.75

Comparison of the results presented in Fig.2 and Fig.3 reveals that nucleation of crystals affect the process significantly. Fig.2 shows the steady state values of both mean crystal sizes L_1 and L_2 as a function of parameter k_e of the primary nucleation rate presented in Eq.(2). The mean values of crystal sizes were computed from the marginal first order moment as

$$\langle L_1 \rangle = \frac{\mu_{1,0}}{\mu_{0,0}} \text{ and } \langle L_2 \rangle = \frac{\mu_{0,1}}{\mu_{0,0}} \qquad (13)$$

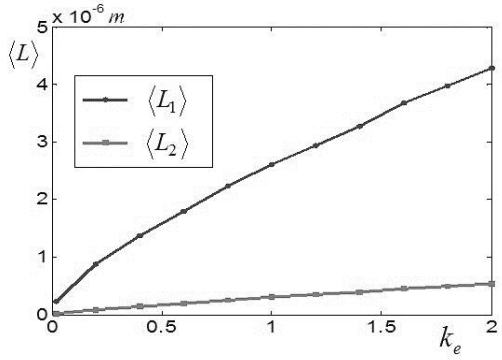


Figure 2. Steady state values of the mean crystal sizes as a function of parameter k_e of the primary nucleation rate

Fig.3 shows that significantly larger crystals are obtained when secondary nucleation is the dominant mechanism producing new crystals. Since the total mass of crystals are of similar values, i.e. in the second case the number of crystals in the final product is much smaller. Fig.4 presents approximations of the steady state marginal population density functions defined as

$$n_{1s}(L_1) = \int_0^\infty n(L_1, L_2) dL_1 \qquad (14)$$

$$n_{2s}(L_2) = \int_0^\infty n(L_1, L_2) dL_2 \qquad (15)$$

and constructed by means of gamma distribution using the joint moments computed.

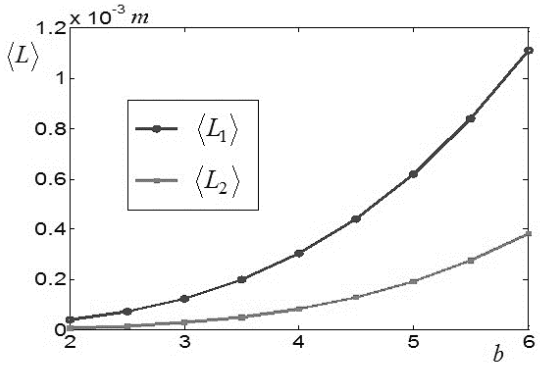


Figure 3. Steady state values of the mean crystal sizes as a function of parameter *b* of the secondary nucleation rate

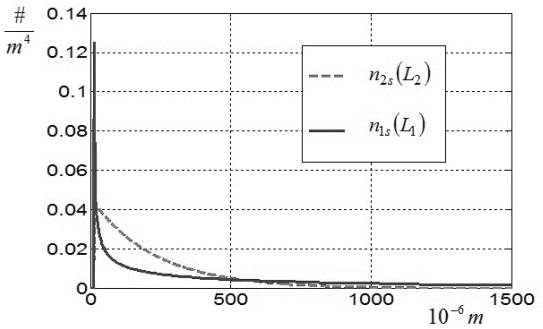


Figure 4. Steady state marginal population density functions when both nucleation rates play role

V. CONCLUSIONS

A two-dimensional population balance model was developed for describing crystallization producing needle-shape crystals. In the model, crystals are characterized by two size dimensions treated as internal variables by means of which the volume of crystals can be computed. An infinite hierarchy of moment equations was developed for the joint moments of size variables by means of which a moment equation reduction, closed at the joint moment providing the partial

volume of crystals in the suspension, was formulated for a cooling crystallizer. The properties and behavior of the bi-dimensional crystal population, approximated by means of the gamma distribution were investigated by simulation.

VI. Acknowledgement

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