A Mathematical Dynamical Model of Distributed Parameters of Continuous Mass Crystallization Process -- Part I: The Construction of Constitutive Equations for Continuous Mass Crystallization Process

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Abstract

Basing on the physico-chemical features of the continuous mass crystallization process according to the literature experiments studies, a mathematical dynamical model of time and space distributed parametres containing composite processes pertaining to the continuous crystallization such as:

- primary nucleation
- crystal growth
- secondary nucleation

has been suggested.

1. Introduction

Several models of the continuous mass crystallization process can be found in literature. However no models of process of mass crystallization can be found which consider the following parameters of continuous mass crystallization process distributed in working space of crystallizer and time:

- primary nucleation / from solution/
- crystal growth / from solution/
- secondary nucleation / through the collision breedings/

from the point of view of the mutual interrelations of these constituent processes. The object is to find common physico-chemical features deciding about the course of the mentioned constituent processes of the continuous mass crystallization. In my doctorate dissertation [1] I have proposed, basing on over 200-quoted papers concerning the continuous mass crystallization, a new method describing this process as an arrangement of double local distributed parameters. The aim of the present article is to show this method as description of the continuous mass crystallization using the medium contact /diffusion, heat transfer, distribution of the field vector velocity/.

2. A concept of double local distributed parameters of the continuous mass crystallization process.

According to [1,2], [3-8], [16-17], [19], [20], the concentration distribution around the growing crystal has a form - Fig.1. From Fig.1. it can be seen that the crystal growth processes are connected with the local distributed parameters. The following phenomena are related to the physico-chemical parameters changes through the reaction of crystal growth around the growing crystal: - diffusion concentration transport, - diffusion energy transport, - energy transport through the heat transfer, - mass and energy transport in the stream of field vector velocity /equations of Marshall, Ranz-Marshall, Frossling [5]/.

Fig.1.

On the other hand, the same features may be defined for the selected volume element of fluid phase in which there is a nucleon" in statu nascendi", as a physico-chemical parameters changes through the nucleation reaction [3-11], [13-18].

Primary nucleation and crystal growth/disturbed through secondary nucleation/ are competitive in the working space of the crystallizer and the residence time of crystals in the crystallizer. Thus, it can be assumed in line with Powers theory [8], that around the growing crystal and nucleon"in statu nacendi" certain fluid/adsorbtion/ layer exist, being connented with the physico-chemical parameters of solution of the working medium. In connection with the fact that the literature of the process of continuous mass crystallization consider the crystal like, a regular mass block in my doctorate disseration

I have proposed the L_x, L_y, L_z- dimensions of this mass block. The fluidal/or adsorbtion/ layer arrangements around the nucleon"in statu nascendi" and growing crystal are assumed to be cuboidal on oriented surfaces $\overrightarrow{F}_{/x,y,z/}$ and $\overrightarrow{F}_{K/x,y,z/}$ surrounding the $\mathfrak{L}_{/x,y,z/}$ /nucleon/ and $\mathfrak{L}_{K/x,y,z/}$ /crystal/ volumes. In my doctorate thesis I have proposed, a new way of description method of the continuous mass crystallization process, as a double local distributed parameters with reactions in two phases - Fig.2. [1,2]

Fig.2.

The points $Q/\xi,\eta,\zeta/ \equiv Q'/\xi';\eta';\zeta'$ / are variable points of the crystallizer working space $\mathfrak{L}_R$ / the so-called variable points/ because the stream balances are in the stationary points $Z/x,y,z/ \equiv K/x,y,z/$ / Green or Neumann function theory/ $Q/\xi,\eta,\zeta/$ - potentional fields /diffusion, heat transfer/

$Q'/\xi';\eta';\zeta'/$ - rotational fields / field vector velocity/

3. Nucleation balances

3.1. Mass balance [1,2]

The mass stream of driving with $\overrightarrow{v}$ velocity volume $\mathfrak{L}_{/x,y,z/}$ in which there is a solution concentration C, has a form:

$$\overrightarrow{j} = C\overrightarrow{v} \qquad \left[\frac{kg}{m2s}\right] \qquad /1/$$

From the point $Q/\xi,\eta,\zeta/$ diffunding in direction $Z/x,y,z/$ stream:

$$\overrightarrow{j_D} = -D_c \operatorname{grad} C \qquad \left[\frac{kg}{m2s}\right] \qquad /2/$$

In point $Z/x,y,z/$ there is the solution concentration decrease through nucleation reaction:

$$v_B = \overline{b/C} - C_s/^i \text{ and } C > C_s \qquad \left[\frac{mol}{s}\right] \qquad /3/$$

With the molar mass G full stream of solution dynamical concentration decreasing value in volume element $\mathfrak{L}_{/x,y,z/}$ can be written as:

$$\frac{\partial}{\partial t}\iiint_{\mathfrak{L}/x,y,z/} C \, d\mathfrak{L}_{/x,y,z/} = \oiint_{F/x,y,z/}\left[D_c \operatorname{grad} C - C\overrightarrow{v}\right]\overrightarrow{dF}_{/x,y,z/} - \iiint_{\mathfrak{L}/x,y,z/} v_B G \, d\mathfrak{L}_{/x,y,z/} \qquad /4/$$

According to the Gauss-Ostrogradzki law, equation /4/ can be written as:

$$\frac{\partial C}{\partial t} = \operatorname{div}\left[D_c \operatorname{grad} C - C\overrightarrow{v}\right] - v_B G \qquad /5/$$

If $D_c \neq D_c /x,y,z,t/$ continuitet equation has form:

$$\frac{\partial C}{\partial t} = \operatorname{grad} C/\operatorname{grad} D_c - \overrightarrow{v}/ \qquad /6/$$

If $D_c \neq D_c /x,y,z,t/$ continuitet equation has a form:

$$\frac{\partial C}{\partial t} = -\overrightarrow{v}\operatorname{grad} C \qquad /7/$$

Continuitet equation /6/ and /7/ can be obtained from /5/ when

$\frac{DC}{Dt} = 0$ /see Appendix 1× and 2× and:

$$\frac{DC}{Dt} = \frac{\partial C}{\partial t} + \operatorname{grad} C/\overrightarrow{v} - \operatorname{grad} D_c/ \qquad /8/$$

The following derivative form of equation /5/ is /see Appendix 1×

$$\frac{DC}{Dt} = D_c\nabla^2 C - C \operatorname{div}\overrightarrow{v} - v_B \cdot G \qquad /9/$$

3.3. Energy balance for nucleation [1,2]

Enthalpy stream of volume $\Omega/x,y,z/$ has a form:

$$\vec{i}_c = C \cdot H \cdot \vec{v} \qquad \left[\frac{J}{m2s}\right] \qquad /10/$$

Heat transfer stream from $Q/\xi, \eta, \zeta/$ to $Z/x,y,z/$ is written as:

$$\vec{i}_l = -\lambda_c \operatorname{grad} T \qquad \left[\frac{J}{m2s}\right] \qquad /11/$$

Enthalpy stream through diffusion from $Q/\xi, \eta, \zeta/$ to $Z/x,y,z/$ in volume $\Omega/x,y,z/$ has a value: $I_D = H_c \iiint_{\Omega/x,y,z/} \left(\operatorname{div}/D_c \operatorname{grad} C/ \right) d\Omega/x,y,z/ \quad \left[\frac{J}{s}\right]$ /12/

Dynamical energy balance value in volume element $\Omega/x,y,z/$ has a form:

$$\frac{\partial}{\partial t} \iiint_{\Omega/x,y,z/} CH\, d\Omega/x,y,z/ = \oint_{F/x,y,z/} \left[\lambda_c \operatorname{grad} T - CH\vec{v} \right] \overrightarrow{dF}/x,y,z/ + H_c \iiint_{\Omega/x,y,z/} \left(\operatorname{div}/D_c \operatorname{grad} C/ \right) d\Omega/x,y,z/ - \iiint_{\Omega/x,y,z/} \left(H_B v_B G \right) d\Omega/x,y,z/ \qquad /13/$$

With application the Gauss-Ostrogradzki law and continuitet equation 3.1.-7 /$\lambda_c \neq \lambda_c/x,y,z,t/$ and $D_c \neq D_c/x,y,z,t/$ /or continuitet equation 3.1.-6 /$\lambda_c = \lambda_c/x,y,z,t/$ and $D_c = D_c/x,y,z,t/$ with $H_c \longrightarrow H/x,y,z,t/$/ equation /13/ can be transformed to the following derivative form:

$$C \frac{DT}{Dt} = \frac{\lambda_c}{c_p} \nabla^2 T - CT \cdot \operatorname{div} \vec{v} - \frac{H_B}{c_p} \cdot v_B G + \frac{H_c}{c_p} \cdot D_c \nabla^2 C \qquad /14/$$

3.3. Impulses balance for nucleation [1,2]

Kinetic energy stream of the solution volume element $\Omega/x,y,z/$ has a form:

$$\vec{N}_c = -\frac{1}{2} \oint_{F/x,y,z/} C \cdot \vec{v} / \overrightarrow{dF}/x,y,z/ \vec{v}/ \qquad [N] \qquad /15/$$

Potential energy stream of the solution volume element $\Omega/x,y,z/$

$$\vec{N}_\Omega = \iiint_{\Omega/x,y,z/} C \vec{g}\, d\Omega/x,y,z/ \qquad [N] \qquad /16/$$

Energy stream solution feeding volume element $\Omega/x,y,z/$

$$\vec{N} = \iiint_{\Omega/x,y,z/} C \vec{v}\, d\Omega/x,y,z/ \qquad \left[\frac{kgm}{s}\right] \qquad /17/$$

Energy stream of viscosity forces of the volume element $\Omega/x,y,z/$

[26], [29,30] :/see Appendix 3/

$$\vec{N}_v = \iiint_{\Omega/x,y,z/} \left[\eta_w \nabla^2 \vec{v} + \frac{\eta_w}{3} \operatorname{grad} \operatorname{div} \vec{v} \right] d\Omega/x,y,z/ \qquad [N] \qquad /18/$$

Dynamical balance of the impulses streams has in volume element $\Omega/x,y,z/$ form:

$$\frac{\partial}{\partial t} \left[\vec{N} \right] = \vec{N}_c + \vec{N}_\Omega + \vec{N}_v \qquad /19/$$

Following derivative form of the dynamical balance of the impulses streams in point $Z/x,y,z/$ of the volume element $\Omega/x,y,z/$:

$$C \frac{D\vec{v}}{Dt} = \eta_w \nabla^2 \vec{v} - C\vec{v} \operatorname{div} \vec{v} + C\vec{g} + \frac{\eta_w}{3} \operatorname{grad} \operatorname{div} \vec{v} \qquad /20/$$

4. Crystal growth balances

According to the fact that the primary nucleation and the crystal growth /disturbed through the secondary nucleation/ are competitive in the working space of the crystallizer and the residence time of crystals in the crystallizer, the circulation of the orientation vectors $\vec{n}/z/$ and $\vec{n}_K/z/$ are in opposition.

From this point of view the sing of the summation the potentional fields/diffusion, heat transfer/ to the rotational field/field vector velocity/ is other in relation to the same of the primary nucleation.

4.1. Growing crystal mass balance [1,2]

In volume element $\Omega_{K/x,y,z/}$ growing crystal takes $\varepsilon/x,y,z/$ volumetric part in solution. Crystal mass stream has a form:

$$\vec{j}_K = \rho_K \cdot \varepsilon \cdot \vec{v}_K \qquad \left[\frac{kg}{m2s}\right] \qquad /21/$$

Diffusion stream from $Q/\xi,\eta,\zeta/$ to $K/x,y,z/$ has a form:

$$\vec{j}_{DK} = - D_K \operatorname{grad}\left[C/1-\varepsilon/\right] \qquad \left[\frac{kg}{m2s}\right] \qquad /22/$$

Increas of the crystal mass is going out through the growth reaction:

$$v_{GK} = \overline{a}/C - C_s/\vec{j}_F/\vec{L}/ \quad \text{and} \quad C > C_s \qquad \left[\frac{mol}{s}\right] \qquad /23/$$

With the crystal molar mass G_K full mass stream of volumetric part of the crystal in volume element $\Omega_{K/x,y,z/}$ can be written as:

$$\frac{\partial}{\partial t}\iiint_{\Omega_{K/x,y,z/}} \varepsilon \rho_K \, d\Omega_{K/x,y,z/} = \oiint_{F_{K/x,y,z/}} \left[\rho_K \varepsilon \vec{v}_K - D_K \operatorname{grad}\left[C/1-\varepsilon/\right]\right] d\vec{F}_{K/x,y,z/} + \iiint_{\Omega_{K/x,y,z/}} /v_{GK} G_K \varepsilon/ d\Omega_{K/x,y,z/} \qquad /24/$$

With the Gauss-Ostrogradzki law equation /24/ can be transformed to:

$$\rho_K \frac{\partial \varepsilon}{\partial t} = \operatorname{div}\left[\rho_K \varepsilon \vec{v}_K - D_K \operatorname{grad}\left[C/1-\varepsilon/\right]\right] + v_{GK} G_K \varepsilon \qquad /25/$$

The following derivative form of the equation /25/ can be obtained as:

$$\frac{D\varepsilon}{Dt} = - \frac{1}{\rho_K} \cdot D_K \nabla^2\left[C/1-\varepsilon/\right] + \varepsilon \operatorname{div} \vec{v}_K + \frac{G_K}{\rho_K} \cdot v_{GK} \varepsilon \qquad /26/$$

4.2. Energy crystal growth balance [1,2]

Enthalpy stream of growing in volume element $\Omega_{K/x,y,z/}$ crystal has a form:

$$\vec{i}_K = \rho_K \varepsilon \vec{v}_K H_K \qquad \left[\frac{J}{m2s}\right] \qquad /27/$$

Crystal heat transfer stream from $Q/\xi,\eta,\zeta/$ to $K/x,y,z/$ in volume element $\Omega_{K/x,y,z/}$:

$$\vec{i}_{KL} = -\lambda_K \operatorname{grad}\left[T_K/1-\varepsilon/\right] \qquad \left[\frac{J}{m2s}\right] \qquad /28/$$

Growing crystal diffusion enthalpy stream has in volume element $\Omega_{K/x,y,z/}$ value:

$$I_{KD} = H_c \iiint_{\Omega_{K/x,y,z/}} \left\{\operatorname{div}\left[-D_K \operatorname{grad}\left[C/1-\varepsilon/\right]\right]\right\} d\Omega_{K/x,y,z/} \qquad \left[\frac{J}{s}\right] \qquad /29/$$

Enthalpy of growing crystal in volume element $\Omega_{K/x,y,z/}$ has a dynamical form:

$$\begin{aligned}\frac{\partial}{\partial t}\iiint_{\Omega_{K/x,y,z/}} \varepsilon \rho_K H_K \, d\Omega_{K/x,y,z/} = \iiint_{\Omega_{K/x,y,z/}} \Big\langle & \operatorname{div}\left\{-\lambda_K \operatorname{grad}\left[T_K/1-\varepsilon/\right]\right\} + \\ & \operatorname{div}\left(\rho_K \varepsilon \vec{v}_K H_K\right) \Big\rangle d\Omega_{K/x,y,z/} + \\ & + H_c \iiint_{\Omega_{K/x,y,z/}} \left\{\operatorname{div}\left[-D_K \operatorname{grad}\left[C/1-\varepsilon/\right]\right]\right\} d\Omega_{K/x,y,z/} + \\ & + H_{GK} \cdot G_K \iiint_{\Omega_{K/x,y,z/}} /v_{GK} \varepsilon/ \, d\Omega_{K/x,y,z/}\end{aligned} \qquad /30/$$

After transformations the same as in 3.2. there is the following derivative form of the crystal temperature:

$$\varepsilon \frac{DT_K}{Dt} = - \frac{\lambda_K}{\rho_K c_{pK}} \nabla^2\left[T_K/1-\varepsilon/\right] + \varepsilon T_K \operatorname{div} \vec{v}_K + \frac{H_{GK} G_K}{c_{pK} \rho_K} \cdot v_{GK} \cdot \varepsilon - \frac{H_c \cdot D_K}{c_{pK} \cdot \rho_K} \nabla^2\left[C/1-\varepsilon/\right]$$

4.3. Growing crystal impulses balance [1,2]

Growing crystal kinetic energy stream of the volume element $\Omega_{K/x,y,z/}$

$$\vec{N}_K = \frac{1}{2} \oint_{F_{K/x,y,z/}} \rho_K \cdot \vec{v}_K / \; d\vec{F}_{K/x,y,z/} \cdot \vec{v}_K / = \iiint_{\Omega_{K/x,y,z/}} \rho_K \cdot / \vec{v}_K \; \mathrm{grad} / \vec{v}_K \cdot \mathcal{E} \, d\Omega_{K/x,y,z/} \quad \left[N \right] \quad /32/$$

Potemtial energy stream of crystal in volume element $\Omega_{K/x,y,z/}$:

$$\vec{N}_{\Omega_K} = \iiint_{\Omega_{K/x,y,z/}} \left[\rho_K \mathcal{E} \vec{g} \right] d\Omega_{K/x,y,z/} + \iiint_{\Omega_{K/x,y,z/}} \left[c/1 - \mathcal{E}/ \vec{g} \right] d\Omega_{K/x,y,z/} \quad \left[N \right] \quad /33/$$

Energy of the growing crystal viscosity forces stream:

$$\vec{N}_{vK} = \iiint_{\Omega_{K/x,y,z/}} \left[\eta_w \cdot \mathcal{E} \cdot \nabla^2 \vec{v}_K + \frac{\eta_w}{3} \cdot \mathcal{E} \cdot \mathrm{grad} \; \mathrm{div} \, \vec{v}_K \right] d\Omega_{K/x,y,z/} \quad \left[N \right] \quad /34/$$

Energy of feeding $\Omega_{K/x,y,z/}$ stream is equal to the crystal own energy since the crystal should float in the solution

$$\vec{N}_f = \vec{v}_K \iiint_{\Omega_{K/x,y,z/}} \left[c/1 - \mathcal{E}/ \right] d\Omega_{K/x,y,z/} = \vec{v}_K \iiint_{\Omega_{K/x,y,z/}} / \rho_K \mathcal{E} / \, d\Omega_{K/x,y,z/} \quad \left[\frac{kgm}{s} \right] \quad /35/$$

Dynamical balance of the impulses streames in point K/x,y,z/ has a form

$$\frac{\partial}{\partial t} \left\{ \vec{N}_f \right\} = \vec{N}_K + \vec{N}_{\Omega K} + \vec{N}_{vK} \quad /36/$$

Following derivative form of the dynamical balance of impulses streams in point $K_{/x,y,z/}$ of the volume element $\Omega_{K/x,y,z/}$ like in 3.3.

$$c/1 - \mathcal{E}/ \frac{\overrightarrow{Dv}}{Dt} = \eta_w \mathcal{E} \nabla^2 \vec{v}_K + \rho_K \mathcal{E} \vec{v}_K \; \mathrm{div} \, \vec{v}_K + \frac{\eta_w}{3} \mathcal{E} \; \mathrm{grad} \; \mathrm{div} \, \vec{v}_K + \left[\rho_K \mathcal{E} + c/1 - \mathcal{E}/ \right] \vec{g} \quad /37/$$

5. Secondary necleation [1, 2] / see Appendix 4 /

According to the literature studies, in my doctorate dissertation [1], I have proposed the new - full description of the secondary nucleation through the crystal energy balance/with literature assumption that collision deformation disappear very fast /in the form:

$$\left[\begin{array}{c} \text{Impact energy} \\ \vec{E}_z \end{array} \right] + \left[\begin{array}{c} \text{Vibration kinetic energy} \\ \vec{E}_k \end{array} \right] = \left[\begin{array}{c} \text{Statical crystal energy} \\ \vec{E}_s \end{array} \right]$$

5.1. Crystal vibration kinetic energy [1, 2]

$$\vec{E}_k = \frac{1}{2} \cdot B \cdot \frac{1}{\rho_K} \cdot \frac{\partial^2 \vec{L}}{\partial t^2} = \frac{1}{2} \cdot B \cdot \frac{1}{\rho_K} \cdot / \frac{\partial^2 L_x}{\partial t^2} + \frac{\partial^2 L_y}{\partial t^2} + \frac{\partial^2 L_z}{\partial t^2} / \left[J \right] \quad /39/$$

5.2. Crystal collision energy [1, 2], [21-24] /see Appendix 4 /

This energy is going out from impact energy of n crystal collisions:

$$\vec{E}_{z/n/} = n \cdot \vec{E}_{z/1/} = n \cdot K_v \cdot \rho_K \cdot \vec{L} \cdot \vec{v}_K^2 \quad \left[J \right] \quad /40/$$

5.3. Statical deformation energy [1, 2], [25-27] /see Appendix 4 /

There are statical hipotetical crystal deformations in the form:

$$\vec{E}_s = h / \nabla^2 \vec{L} + \frac{k}{k - 2} \; \mathrm{grad} \; \mathrm{div} \, \vec{L} / \quad \left[J \right] \quad /41/$$

5.4. Dynamical energy balance on crystal surface has a form [1, 2] / see Appendix 4 /

$$n \cdot K_v \cdot \rho_K \cdot \vec{L} \cdot \vec{v}_K^2 + \frac{1}{2} \cdot \frac{B}{\rho_K} \cdot \frac{\partial^2 \vec{L}}{\partial t^2} = h / \nabla^2 \vec{L} + \frac{k}{k-2} \; \mathrm{grad} \; \mathrm{div} \, \vec{L} / \quad /42/$$

6. The discussion of the equations mathematical model with distributed parameteres of the continuous mass crystallization

The equations of the primary nucleation process:

$$\mathrm{I} \left| \begin{array}{l} \frac{DC}{Dt} = D_c \nabla^2 C - C \; \mathrm{div} \, \vec{v} - v_B' G \quad /1/ \\ C \frac{DT}{Dt} = \frac{\lambda_c}{c_p} \nabla^2 T - C \cdot T \cdot \mathrm{div} \, \vec{v} - \frac{H_B}{c_p} \cdot v_B' G + \frac{H_c}{c_p} \cdot D_c \nabla^2 C \quad /2/ \end{array} \right.$$

$$C\frac{\overrightarrow{Dv}}{Dt} = \eta_w \nabla^2 \overrightarrow{v} - C\overrightarrow{v}\,\mathrm{div}\,\overrightarrow{v} + C\overrightarrow{g} + \frac{\eta_w}{3}\,\mathrm{grad}\,\mathrm{div}\,\overrightarrow{v} \qquad /3/$$

The equations of the crystal growth process:

$$\frac{D\varepsilon}{Dt} = -\frac{1}{\rho_K} D_K \nabla^2 \left[C/1-\varepsilon/\right] + \varepsilon\,\mathrm{div}\,\overrightarrow{v_K} + \frac{G_K}{\rho_K}\cdot v_{GK}\,\varepsilon \qquad /1'/$$

$$\text{II}\left|\frac{DT_K}{Dt} = -\frac{\lambda_K}{\rho_K c_{pK}}\nabla^2\left[T_K/1-\varepsilon/\right] + \varepsilon T_K\,\mathrm{div}\,\overrightarrow{v_K} + \frac{H_{GK}}{c_{pK}}\cdot\frac{G_K}{\rho_K} v_{GK}\,\varepsilon \to \frac{H_c D_K}{\rho_K c_{pK}}\nabla^2\left[C/1-\varepsilon/\right]\right. \qquad /2'/$$

$$C/1-\varepsilon/\frac{\overrightarrow{Dv}}{Dt} = \eta_w\varepsilon\nabla^2\overrightarrow{v_K} + \rho_K\varepsilon\overrightarrow{v_K}\,\mathrm{div}\,\overrightarrow{v_K} + \left[\rho_K\varepsilon + C/1-\varepsilon/\right]\overrightarrow{g} + \frac{\eta_w}{3}\varepsilon\,\mathrm{grad}\,\mathrm{div}\,\overrightarrow{v_K} \qquad /3'/$$

In the equations of crystal growth there is a function of growth reaction - v_{GK}, which is not only a function of supersaturation/$C-C_s$/ but also of the crystal size $\overrightarrow{f/L/}$. I have modified this literature form of crystal growth solving an equation /42/ due to $\overrightarrow{L/L_x}$, L_y, L_z/. By solving a dynamical equation $\overrightarrow{L}$ in the form

$$\text{III}\left|n\rho_K K_v \overrightarrow{L}\overrightarrow{v_K}^2 + \frac{B}{2\rho_K}\frac{\partial^2\overrightarrow{L}}{\partial t^2} = h\nabla^2\overrightarrow{L} + \frac{k}{k-2}\,\mathrm{grad}\,\mathrm{div}\,\overrightarrow{L}\right.$$

the crystal growth function is modified considerably in equations II-1', II-2'. In its turn equation III is related through crystal velocity to crystal growth equation II-3'. The crystal growth is medium connected through mass and energy diffusion transport. The interrelation of the same type is observed between equations I-1 and I-2 due to II-1' and II-2' because:

$$\nabla^2\left[C/1-\varepsilon/\right] = /1-\varepsilon/\nabla^2 C - C\nabla^2\varepsilon \qquad /1/$$

and

$$\nabla^2\left[/1-\varepsilon/T_K\right] = T_K\nabla^2\left[/1-\varepsilon/\right] + /1-\varepsilon/\nabla^2 T_K \qquad /2/$$

In equations /1,2/ there is a part of fluid phase and a part o crystal phase. The fluid phase; $/1-\varepsilon/\nabla^2 C$ and $T_K\nabla^2$ $/1-\varepsilon/$. The crystal phase; $-C\nabla^2\varepsilon$ and $/1-\varepsilon/\nabla^2 T_K$. Since the fluid phase nucleation "in statu nascendi" has to be described by equations I - 1,2,3 , the crystal growth equations have a form:

$$\frac{D\varepsilon}{Dt} = +\frac{1}{\rho_K} D_K \cdot C\nabla^2\varepsilon + \varepsilon\,\mathrm{div}\,\overrightarrow{v_K} + \frac{G_K}{\rho_K}\cdot\varepsilon\cdot v_{GK} \qquad /1''/$$

$$\text{II}\left|\varepsilon\frac{DT_K}{Dt} = -\frac{\lambda_K}{\rho_K c_{pK}}/1-\varepsilon/\nabla^2 T_K + \varepsilon T_K\,\mathrm{div}\,\overrightarrow{v_K} + \frac{H_{GK}}{c_{pK}}\cdot\frac{G_K}{\rho_K}\varepsilon\cdot v_{GK} + \frac{H_c\cdot D_K}{\rho_K\cdot c_{pK}}\cdot C\nabla^2\varepsilon\right. \qquad /2''/$$

$$C/1-\varepsilon/\frac{\overrightarrow{Dv}}{Dt} = \eta_w\varepsilon\nabla^2\overrightarrow{v_K} + \rho_K\varepsilon\overrightarrow{v_K}\,\mathrm{div}\,\overrightarrow{v_K} + \frac{\eta_w}{3}\varepsilon\,\mathrm{grad}\,\mathrm{div}\,\overrightarrow{v_K} + \left[\rho_K\varepsilon + C/1-\varepsilon/\right]\overrightarrow{g} \qquad /3''/$$

The above mentioned relations between the constituent processes of the continuous mass crystallization process: primary nucleation, crystal growth and the secondary nucleation can be considered as parameters $/C_o, T_o, \overrightarrow{v_o}/$ and $/\varepsilon_o, T_{Ko}, \overrightarrow{v_{Ko}}, \overrightarrow{L_o}/$ correspondent to those of the initial stage of crystallization in points Z/x,y,z/ and K/x,y,z/. Factors/C,T,$\vec{V}$/ and /$\varepsilon, T_K, \overrightarrow{v_K}, \overrightarrow{L}$/ are resultant magnitudes of the process. Input-Output of the continuous mass crystallization is shown by figure 3. Fig.3. 7. Conclusion.

The introduction of the following derivatives into all the equations aims to fulfil the conditions of constitutive invariance due to direction Q⟶Z and Q⟶K and geometrical coordinates transformation into mass coordinates, energy

coordinates and the coordinates of the fields vectors velocity. The derived equations make use of phenomenon relation occuring inside the working medium of the crystallization process. These equations are valid due to optimal working medium since in Eucledian space in Carthesian coordinates the vector components are the same for correspondent covariance and contravariance tensors. In my doctorate dissertation [1] I have solved the systems of equations I, II and III basing on the field theory and Green function theory.[xx]

Notation

C - concentration [kg hydrate/m^3 solution]
C_s - saturation concentration of solute kg/m^3
b - coefficient of nucleation
a - coefficient of crystal growth
G - molar mass of solution $kg/molm^3$
G_K - molar mass of crystal $kg/molm^3$
i - kinetic order of nucleation
j - kinetic order of crystal growth
T - solution temperature ^oK
T_K - crystal temperature ^oK
ε - volumetric crystal part in solution [crystal volume/ solution volume]
$1-\varepsilon$ - volumetric part of solution
$\vec{L}$ - crystal size vector m
H_c - specific enthalpy of solution J
H_B - nucleation specific enthalpy J
H_{GK} - crystal growth specific enthalpy J
D_c - diffusion coefficient solution-solution $[m^2/s]$
D_K - diffusion coefficient crystal-solution $[m^2/s]$
λ_c - heat transfer coefficient solution-solution $J/m^2 s\,^oK$
λ_K - heat transfer coefficient crystal-solution $J/m^2 s\,^oK$
c_p - specific heat of solution $J/kg\,^oK$
c_{pK} - specific heat of crystal $J/kg\,^oK$
ϱ_K - specific crystal density kg/m^3
H - enthalpy of the solution J
H_K - enthalpy of the crystal J
K_V - volumetric crystal shape factor
K_A - surface crystal shape factor
n - statistical crystal collision number
k - Poisson constant
h - crystal press module N/m^2
B - function of / $\eta_w, \vec{L}, \varepsilon, K_V, K_A$, crystal dusting/ $[kg/m^3]^2$
v_B - nucleation reaction mol/s
v_{GK} - crystal growth reaction mol/s
$\mathfrak{V}_R$ - volume of crystallizer m^3
a, b, c - dimensions of the $\mathfrak{V}_R$ - primary nucleation m
$\mathfrak{V}_K$ - crystal growth and secondary nucleation
η_w - dynamic viscosity coefficient kg/m^3
$\vec{v}$ - solution velocity vector m/s
$\vec{v}_K$ - crystal velocity vector m/s
$\vec{g}$ - gravitational constant m/s^2

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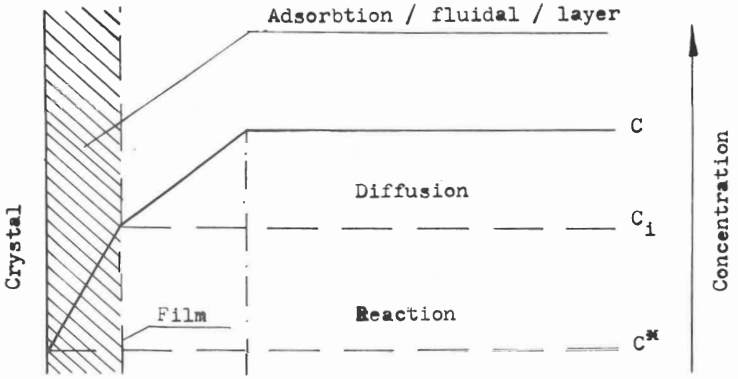

Fig.1. The concentration distribution around the growing crystal .
C - bulk concentration, C_i - interphase concentration, C^* - crystal surface concentration

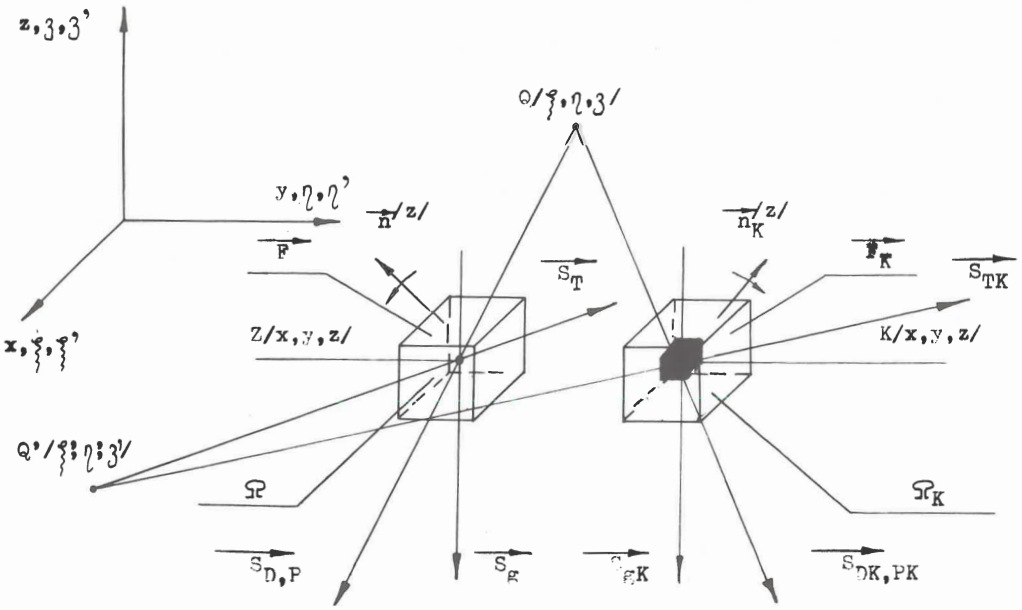

Fig.2. A double local distribute parameter method as a new way to describe the continuous mass crystallization process [1].
$\vec{n}/z/, \vec{n}_K/z/$ - normal volume orientation vector for nucleation, for crystal growth
$\vec{S}_D, \vec{P}, \vec{S}_{DK}, \vec{P}_K$ - diffusion/heat transfer stream for nucleation, for crystal growth
$\vec{S}_g, \vec{S}_{gK}$ - gravity force stream for nucleon, for crystal growth
$\vec{S}_T, \vec{S}_{TK}$ - turbulence stream for nucleon "in statu nascendi" velocity vector, for crystal growth velocity vector.

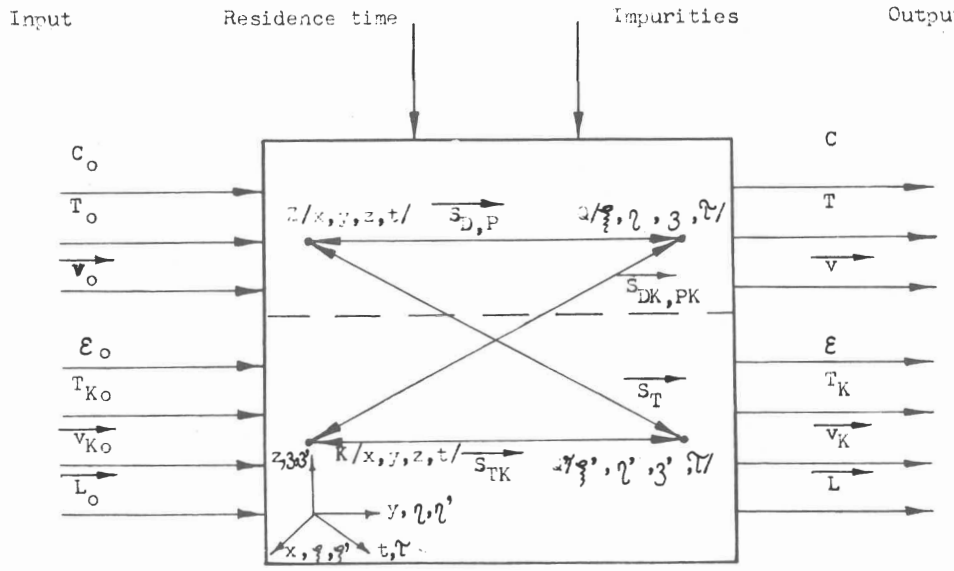

Fig.3. Input- Output for continuous mass crystallization process.