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ENTROPY PRODUCTION IN THE STATIONARY EUTECTIC GROWTH

The entropy production per unit time is calculated for the regular lamellae -, and for the regular rods formation, respectively. The entropy production is a function of some parameters which define the eutectic phase diagram, coefficient of the diffusion in the liquid, and some capillary parameters connected with the mechanical equilibrium located at the triple point of the solid/liquid interface. Minimization of the entropy production allowed to formulate mathematically the so-called *Growth Law* for both envisaged eutectic morphologies.

Keywords: Regular eutectics growth; Entropy production; Criterion of minimum entropy production; Growth Law

Notations

- D coefficient of diffusion in the liquid, [m²/s],
- k_S equilibrium partition ratio for a given eutectic phase, $S = \alpha, \beta$, [at.%/at.%],
- L_S latent heat of a given eutectic phase, $S = \alpha, \beta, [J/m^3]$,
- m_S slope of a given *liquidus* line, $S = \alpha, \beta$, [K/mole.fr.],
- N solute concentration, [at.%],
- N_E eutectic concentration of the solute, [at.%],
- N_0 nominal solute concentration in a given alloy, [at.%],
- R_S radius of a given eutectic phase curvature, $S = \alpha, \beta$, [m],
- S_{α} half the width of the α eutectic phase lamella, [m],
- S_{β} half the width of the β eutectic phase lamella, [m],
- T temperature, [K],
- v crystal growth rate, [m/s],
- V volume, [m³],
- V_S volume fraction of a given eutectic phase, $S = \alpha, \beta$, [dimensionless],
- δT undercooling of the s/l interface, [K],
- σ_S specific surface free energy of a given phase's interface, $S = \alpha, \beta, [J/m^2],$
- $\sigma_{\alpha/\beta}$ boundary free energy (between α –, and β eutectic phase), [J/m²].

1. Introduction

The growth of the (Zn) single crystal strengthened by the $E = (Zn) + Zn_{16}Ti$ – eutectic precipitate was performed by the *Bridgman's* system. Experimentally, the strengthening layers (stripes) are generated periodically in the (Zn) – single crystal as a result of the cyclical course of precipitation which accompanies the directional solidification. These layers evince diversified eutectic morphologies like irregular rods, regular lamellae, and regular rods. Transformations of the mentioned structures (one into other) were observed at some threshold growth rates. It is obvious that the eutectic structures formation is subjected to the competition.

Thus, it is postulated that the thermodynamics of irreversible processes is able to explain / justify the structural transformations. However, first of all, the criterion of the minimum entropy production is to be applied.

The criterion is: the regular eutectic structure evinces one and only one spacing, when the imposed growth rate and thermal gradient at the s/l interface are constant; it means that solidification proceeds at minimum entropy production.

An application of such a criterion involves the calculation of the entropy production per unit time for both eutectic regular structures: lamellar structure and rod-like structure and subsequently, it requires to subject the entropy production to minimization in order to formulate the *Growth Law* for considered structures.

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The (Zn) – single crystal growth proceeds in a stationary state in the *Bridgman's* system with constant both the v – growth rate and $G = \partial T/\partial z$ – thermal gradient. Thus, the application of the criterion of *minimum entropy production* is justified in this situation.

After some rearrangements and in a general form, [1], entropy production per unit time and unit volume associated with the mass transfer is given as follows:

$$\sigma_D = \frac{DR_g \psi}{N_i (1 - N_i)} |grad.N_i|^2 \quad T \equiv T_{s/l} = const.$$
(1)

Eq. (1) is ready to be introduced into Eq. (2) in order to calculate entropy production per unit time, separately for lamellar -, and rod-like eutectic structure formation within the layers strengthening the (Zn) – single crystal. R_g , is the gas constant and, ψ , the thermodynamic factor.

$$P_D = \int_V \sigma_D \, dV \tag{2}$$

The current description is connected with the mass transfer in the liquid adjacent to the s/l interface but contained in the diffusion zone: $z_D \approx D/v$ (in the z – direction). Entropy production associated with the heat transfer is neglected, ($\sigma_T = 0$).

The V – volume is the key parameter for the subsequent calculation / solution of the integral, Eq. (2). It leads to the separation of integration which now, will be made simultaneously for the lamellar -, and rod-like structure formation. The V – volume has already been defined for the lamellar -, and the rod-like structure formation, [1].

The V – volume is reproduced periodically in the regular eutectic morphology. However, this volume is not the same for every new solidification rate. Therefore, the average entropy production should be calculated:

a) for the lamellar eutectic growth

$$\overline{P}_D^L = \frac{1}{S_{\alpha} + S_{\beta}} \int_V \sigma_D dV$$
(3a)

b) for the rod-like eutectic growth

$$\overline{P}_D^R = \frac{1}{\pi \left(r_\alpha + r_\beta \right)^2} \int_V \sigma_D \, dV \tag{3b}$$

Finally, Eq. (4) is obtained by introducing Eq. (1) into Eq. (2):

$$P_D = \frac{DR_g \psi}{N_i \left(1 - N_i\right)} \int_V \left| grad. N_i \right|^2 dV$$
(4)

2. Calculation of the entropy production per unit time

Taking into account that the entropy production will be subjected to minimization, the $DR_g\psi/[N_i(1 - N_i)]$ – term in Eq. (4) can be neglected because it is constant.

The volume integral, Eq. (4), is transformed into a double integral according to the *Green-Ostrogradski's* theorem, $(N_i \equiv N^L;$

$$\nabla^2 N^L \equiv \nabla^2 \delta N^L$$
; grad. $N^L \equiv$ grad. δN^L ; $\frac{dN^L}{dn} \equiv \frac{d\delta N^L}{dn}$). After

the theorem application, Eq. (4) is transformed into:

a) for the lamellar structure formation

$$\int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| \operatorname{grad.} N^{L}(x,z) \right|^{2} dz \, dx = \frac{v}{2D} \int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \frac{d\left[\delta N^{L}(x,z)\right]^{2}}{dz} dz \, dx + \int_{K_{1}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} dA + \int_{K_{2}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} dA + \int_{K_{3}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} dA + \int_{K_{3}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} dA + \int_{K_{4}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} dA + (5a)$$

with the validity of the scheme shown in Fig. 1a,

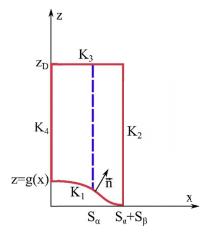


Fig. 1a. Contours applied to Eq. (5a)

$$K_{1} \in x = x, \ z = g\left(x\right) \quad x \in \left[0, S_{\alpha} + S_{\beta}\right]$$

$$K_{2} \in x = S_{\alpha} + S_{\beta}, \ z = z \quad z \in \left[g\left(S_{\alpha} + S_{\beta}\right), \ z_{D}\right]$$

$$K_{3} \in x = x, \ z = z_{D} \quad x \in \left[S_{\alpha} + S_{\beta}, 0\right]$$

$$K_{4} \in x = 0, \ z = z \quad x \in \left[z_{D}, g\left(S_{\alpha} + S_{\beta}\right)\right] \quad (6a)$$

Additionally,

$$dA = \sqrt{1 + \left[g'(x)\right]^2} \tag{7a}$$

In an approximation, $N^L = N_E$, $\frac{\partial N^L}{\partial z} = 0$, $\frac{\partial N^L}{\partial x} = 0$, for $z = z_D$; $\frac{\partial N^L}{\partial x} = 0$, for x = 0, and $x = S_{\alpha} + S_{\beta}$; in accordance with the

field of the solute concentration, $N^L(x, z)$, which yields from the solution to the diffusion equation, [2]. Thus, Eq. (5a) becomes:

$$\int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| \operatorname{grad.} N^{L}(x,z) \right|^{2} dz \, dx =$$

$$\frac{v}{2D} \int_{0}^{S_{\alpha}+S_{\beta}} \left[\left(\delta N^{L}(x,z_{D}) \right)^{2} - \left(\delta N^{L}(x,g(x)) \right)^{2} \right] dx +$$

$$\int_{0}^{S_{\alpha}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} \sqrt{1 + \left(g'(x)\right)^{2}} \, dx +$$

$$\int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,z) \frac{\partial N^{L}(x,z)}{\partial n} \sqrt{1 + \left(g'(x)\right)^{2}} \, dx \quad (8a)$$

Moreover, it is assumed that,

$$\frac{\partial N^{L}(x,z)}{\partial n}\bigg|_{z=g(x)} = -\frac{v_{n}}{D}\delta N^{L}(x,z)$$
(9a)

then,

$$\int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| \operatorname{grad.} N^{L}(x,z) \right|^{2} dz \, dx = -\frac{v}{2D} \int_{0}^{S_{\alpha}+S_{\beta}} \left[\delta N^{L}(x,g(x)) \right]^{2} dx + \int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) \frac{v}{D} \left(\frac{N^{L}(x,g(x)) - N^{\alpha}(x,g(x))}{N^{\alpha}(x,g(x))} \right) dx + \int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) \frac{v}{D} \left(\frac{N^{L}(x,g(x)) - N^{\alpha}(x,g(x))}{N^{\beta}(x,g(x))} \right) dx \quad (10a)$$

The integral, Eq. (10a) is now connected directly with the *Bridgman's* system technology and eutectic phase diagram, Fig. 2.

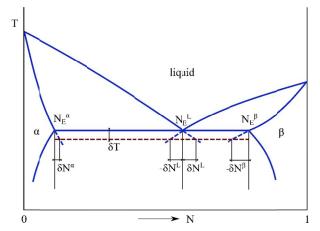


Fig. 2. Arbitrary eutectic phase diagram presenting the definition of some parameters associated with the non-equilibrium solidification and an accompanying undercooling of the s/l interface; $\delta T_{\alpha} = \delta T_{\beta} \equiv \delta T$

The considered solidification process is assumed to occur near equilibrium, Fig. 2, in order to ensure the validity of linear thermodynamics, [3]. In fact, a small deviation from equilibrium is considered by imposing some moderate values of growth rate, that is, $0 < v \le v_3$, in the examined experiment.

The parameters defined by the phase diagram, Fig. 2, are:

$$N^{L} = N_{E}^{L} \pm \delta N^{L}, \ N^{\alpha} = N_{E}^{\alpha} + \delta N^{\alpha}, \ N^{\beta} = N_{E}^{\beta} - \delta N^{\beta}$$
(11)

Combination of the definitions, Eq. (11), and Eq. (10), yields:

$$\int_{0}^{S_{a}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| grad. N^{L}(x,z) \right|^{2} dz dx =$$

$$= -\frac{v}{2D} \int_{0}^{S_{a}+S_{\beta}} \left[\delta N^{L}(x,g(x)) \right]^{2} dx +$$

$$\frac{v}{D} \int_{0}^{S_{a}} \delta N^{L}(x,g(x)) \left[\frac{N_{E}^{L}-N_{E}^{\alpha}+\delta N^{L}(x,g(x))-}{\delta N^{\alpha}(x,g(x))} \right] dx +$$

$$\frac{v}{D} \int_{S_{a}}^{S_{a}+S_{\beta}} \delta N^{L}(x,g(x)) \left[\frac{N_{E}^{L}-N_{E}^{\beta}+\delta N^{L}(x,g(x))-}{\delta N^{\beta}(x,g(x))} \right] dx \quad (12a)$$

Subsequently,

$$\int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| grad.N^{L}(x,z) \right|^{2} dz dx =$$

$$\frac{v}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} \right) \int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) dx + \left(N_{E}^{L} - N_{E}^{\beta} \right) \int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,g(x)) dx \right] -$$

$$\frac{v}{D} \left[\int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) \delta N^{\alpha}(x,g(x)) dx + \int_{S_{\alpha}+S_{\beta}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,g(x)) \delta N^{\beta}(x,g(x)) dx \right] +$$

$$\frac{v}{2D} \int_{0}^{S_{\alpha}+S_{\beta}} \left[\delta N^{L}(x,g(x)) \right]^{2} dx \qquad (13a)$$

Eq. (13a) presents the solution to the integral, Eq. (4), over the z – variable.

b) for the rod-like structure formation

$$\begin{aligned} & \iiint_{V} \left| grad. N^{L} \left(x, y, z \right) \right|^{2} dV = \\ & \frac{v}{2D} \iint_{K} \left\{ \left[\delta N^{L} \left(x, y, z_{D} \right) \right]^{2} - \\ & \left\{ \left[\delta N^{L} \left(x, y, g \sqrt{x^{2} + y^{2}} \right) \right]^{2} \right\} dz \, dx + \\ & \iint_{\mathcal{A}_{1}} \delta N^{L} \left(x, y, z \right) \frac{\partial N^{L} \left(x, y, z \right)}{\partial n} dA + \end{aligned} \tag{5b}$$





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$$\iint_{A_{2}} \delta N^{L}(x, y, z) \frac{\partial N^{L}(x, y, z)}{\partial n} dA +$$
$$\iint_{A_{3}} \delta N^{L}(x, y, z) \frac{\partial N^{L}(x, y, z)}{\partial n} dA$$
(5b ctn)

with the validity of the scheme shown in Fig. 1b.

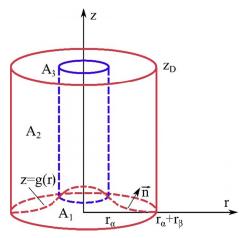


Fig. 1b. Surfaces applied to Eq. (5b), $A = A_1 \cup A_2 \cup A_3$

$$A_{1} = \left\{ \left(x, y, g\left(\sqrt{x^{2} + y^{2}}\right)\right) : \sqrt{x^{2} + y^{2}} \le r_{\alpha} + r_{\beta} \right\}$$

$$A_{2} = \left\{ \left(x, y, g\left(r_{\alpha} + r_{\beta}\right)\right) : \sqrt{x^{2} + y^{2}} = r_{\alpha} + r_{\beta} \right\}$$

$$A_{3} = \left\{ \left(x, y, z_{D}\right) : \sqrt{x^{2} + y^{2}} \le r_{\alpha} + r_{\beta} \right\}$$

$$K = \left\{ \left(x, y\right) : \sqrt{x^{2} + y^{2}} \le r_{\alpha} + r_{\beta} \right\}$$
(6b)

Additionally,

$$V = \begin{cases} \left(x, y, z\right) : \sqrt{x^2 + y^2} \le r_{\alpha} + r_{\beta}, \\ g\left(\sqrt{x^2 + y^2}\right) \le z \le z_D \end{cases}$$
(7b)

In an approximation, $N^L = N_E$, $\frac{\partial N^L}{\partial z} = 0$, $\frac{\partial N^L}{\partial r} = 0$, for $z = z_D$; $\frac{\partial N^L}{\partial r} = 0$, for r = 0, and $r = r_{\alpha} + r_{\beta}$; in accordance with the field of the solute concentration, $N^L(r, z)$, which yields from the solution to the diffusion equation, [2]. Thus, Eq. (5b) becomes:

$$\iiint_{V} \left| \operatorname{grad.} N^{L}(x, y, z) \right|^{2} dV = -\frac{v}{2D} \iint_{K} \left[\delta N^{L}(x, y, z) \right]^{2} dz \, dx + \iint_{A_{1}} \delta N^{L}(x, y, z) \frac{\partial N^{L}(x, y, z)}{\partial n} dA$$
(8b)

In this coordinate system: $\delta N^L(r \cos \varphi, r \sin \varphi, g(r)) \Rightarrow \delta N^L(r, g(r))$, next. It allows to transform Eq. (8b) into:

$$\iiint_{V} \left| grad. N^{L}(x, y, z) \right|^{2} dV = \frac{2\pi v}{2D} \int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr + 2\pi \int_{0}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) \frac{\partial N^{L}(r, g(r))}{\partial n} \sqrt{1 + \left(\frac{\partial g(r)}{\partial r}\right)^{2}} r dr \quad (8b')$$

Moreover, it is assumed that,

$$\frac{\partial N^{L}(r,g(r))}{\partial n}\bigg|_{z=g(r)} = -\frac{v_{n}}{D}\delta N^{L}(r,g(r))$$
(9b)

then,

$$\begin{aligned} & \iiint_{V} \left| grad. N^{L} \left(x, y, z \right) \right|^{2} dV = \\ & - \frac{2 \pi v}{2D} \int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L} \left(r, g\left(r \right) \right) \right]^{2} r \, dr + \\ & \frac{2 \pi v}{D} \int_{0}^{r_{\alpha}} \delta N^{L} \left(r, g\left(r \right) \right) \left[\frac{N^{L} \left(r, g\left(r \right) \right) - }{N^{\alpha} \left(r, g\left(r \right) \right)} \right] r \, dr + \\ & \frac{2 \pi v}{D} \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L} \left(r, g\left(r \right) \right) \left[\frac{N^{L} \left(r, g\left(r \right) \right) - }{N^{\beta} \left(r, g\left(r \right) \right)} \right] r \, dr \quad (10b)
\end{aligned}$$

Combination of the definitions, Eq. (11), with Eq. (10b), yields:

$$\begin{aligned} & \iiint_{V} \left| grad. N^{L}(x, y, z) \right|^{2} dV = \\ & \frac{2 \pi v}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} \right)_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) r dr + \\ & \left(N_{E}^{L} - N_{E}^{\beta} \right)_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) r dr \right] - \\ & \frac{2 \pi v}{D} \left[\int_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) \delta N^{\alpha}(r, g(r)) r dr + \\ & \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) \delta N^{\beta}(r, g(r)) r dr \right] + \\ & \frac{2 \pi v}{2 D} \int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr \end{aligned} \tag{13b}$$

Both integrations for lamellar -, and rod-like structure were performed considering the eutectic phase diagram, and particularly, deviation from the thermodynamic equilibrium. The $\delta T(v)$ – undercooling of the s/l interface, Fig. 2, imposed on the process under investigation, responsible for this deviation, is equal to: $\delta T(0) = 0$, for the equilibrium state itself.





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Consequentially, the integration over the x – variable is to be performed:

a) effect of the capillary parameters on the lamellar structure formation

The integral,

$$\int_{0}^{S_{\alpha}+S_{\beta}} \int_{g(x)}^{z_{D}} \left| grad. N^{L}(x,z) \right|^{2} dz dx =$$

$$\frac{v}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} \right) \int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) dx + \left(N_{E}^{L} - N_{E}^{\beta} \right) \int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,g(x)) dx \right] -$$

$$\frac{v}{D} \left[\int_{0}^{S_{\alpha}} \delta N^{L}(x,g(x)) \delta N^{\alpha}(x,g(x)) dx + \int_{S_{\alpha}+S_{\beta}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,g(x)) \delta N^{\beta}(x,g(x)) dx \right] +$$

$$\frac{v}{2D} \int_{0}^{S_{\alpha}+S_{\beta}} \left[\delta N^{L}(x,g(x)) \right]^{2} dx \qquad (13a)$$

contains three unknowns: $\delta N^L(x, g(x)), \delta N^a(x, g(x)), \delta N^\beta(x, g(x))$. In this situation, the following definition associated with the s/l interface undercooling can be applied:

$$\delta N^{\alpha} \left(x, g(x) \right) = k_{\alpha} \, \delta N^{L} \left(x, g(x) \right) + \frac{k_{\alpha}}{m_{\alpha}} \frac{T_{E}}{L_{\alpha}} \sigma_{\alpha}^{L} \left(x, g(x) \right) \frac{1}{R_{\alpha} \left(x, g(x) \right)}$$
(14a)

with,

$$\frac{1}{R_{\alpha}\left(x,g\left(x\right)\right)} = \widehat{K}_{\alpha}\left(x,g\left(x\right)\right)$$
(15a)

After some simplifications, Eq. (15a) becomes:

$$\widehat{K}_{\alpha}\left(x,g\left(x\right)\right) = \widehat{K}_{\alpha} = \frac{\sin\theta_{\alpha}^{L}}{S_{\alpha}} = const.$$
 (16a)

Analogously,

$$\delta N^{\beta} \left(x, g(x) \right) = k_{\beta} \, \delta N^{L} \left(x, g(x) \right) + \frac{k_{\beta}}{m_{\beta}} \frac{T_{E}}{L_{\beta}} \sigma_{\beta}^{L} \left(x, g(x) \right) \frac{1}{R_{\beta} \left(x, g(x) \right)}$$
(17a)

with,

$$\frac{1}{R_{\beta}(x,g(x))} = \hat{K}_{\beta}(x,g(x))$$
(18a)

After some simplifications, Eq. (18a) becomes:

$$\widehat{K}_{\beta}\left(x,g\left(x\right)\right) = \widehat{K}_{\beta} = \frac{\sin\theta_{\beta}^{L}}{S_{\beta}} = const.$$
 (19a)

Additional simplifications are as follows:

$$\sigma_{\alpha}^{L}(x,g(x)) = \sigma_{\alpha}^{L} = const.,$$

and $\sigma_{\beta}^{L}(x,g(x)) = \sigma_{\beta}^{L} = const.$ (20a)

$$\frac{1}{m_{\alpha}} \frac{T_E}{L_{\alpha}} \sigma_{\alpha}^L = A_{\alpha}, \text{ and } \frac{1}{m_{\beta}} \frac{T_E}{L_{\beta}} \sigma_{\beta}^L = A_{\beta}$$
(21a)

Insertion of the above simplifications into Eq. (13a) leads to:

$$P_{D}^{L} = \frac{v}{D} \begin{bmatrix} \left(N_{E}^{L} - N_{E}^{\alpha}\right) \int_{0}^{S_{\alpha}} \delta N^{L}(x, g(x)) dx + \\ \left(N_{E}^{L} - N_{E}^{\beta}\right) \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \delta N^{L}(x, g(x)) dx \end{bmatrix} - \frac{v}{D} \begin{bmatrix} k_{\alpha} \int_{0}^{S_{\alpha}} \left[\delta N^{L}(x, g(x)) \right]^{2} dx + \\ k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} \int_{0}^{S_{\alpha}} \delta N^{L}(x, g(x)) dx + \\ k_{\beta} \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L}(x, g(x)) \right]^{2} dx + \\ k_{\beta} A_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}} \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \delta N^{L}(x, g(x)) dx \end{bmatrix} + \frac{v}{2D} \begin{bmatrix} \int_{0}^{S_{\alpha}} \left[\delta N^{L}(x, g(x)) \right]^{2} dx + \\ \int_{S_{\alpha} + S_{\beta}} \left[\delta N^{L}(x, g(x)) \right]^{2} dx + \\ \int_{S_{\alpha} + S_{\beta}} \left[\delta N^{L}(x, g(x)) \right]^{2} dx + \end{bmatrix}$$
(22a)

 effect of the capillary parameters on the rod-like structure formation The integral,

$$\begin{aligned}
& \iiint_{V} \left| grad. N^{L}(x, y, z) \right|^{2} dV = \\
& \frac{2\pi\nu}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} \right)_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) r dr + \\
& \left(N_{E}^{L} - N_{E}^{\beta} \right)_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) r dr \right] - \\
& \frac{2\pi\nu}{D} \left[\int_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) \delta N^{\alpha}(r, g(r)) r dr + \\
& \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) \delta N^{\beta}(r, g(r)) r dr \right] + \\
& \frac{2\pi\nu}{2D} \int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr \end{aligned} \tag{13b}$$

contains three unknowns: $\delta N^L(r, g(r))$, $\delta N^{\alpha}(r, g(r))$ and $\delta N^{\beta}(r, g(r))$. In this situation, the following definition associated with the s/l interface undercooling can be applied:

$$\delta N^{\alpha}(r,g(r)) = k_{\alpha} \, \delta N^{L}(r,g(r)) + \frac{k_{\alpha}}{m_{\alpha}} \frac{T_{E}}{L_{\alpha}} \sigma_{\alpha}^{L}(r,g(r)) \frac{1}{R_{\alpha}(r,g(r))}$$
(14b)



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with,

$$\frac{1}{R_{\alpha}\left(r,g\left(r\right)\right)} = \hat{K}_{\alpha}\left(r,g\left(r\right)\right)$$
(15b)

After some simplifications, Eq. (15b) becomes:

$$\widehat{K}_{\alpha}\left(r,g\left(r\right)\right) = \widehat{K}_{\alpha} = \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}} = const.$$
 (16b)

Analogously,

$$\delta N^{\beta}(r,g(r)) = k_{\beta} \, \delta N^{L}(r,g(r)) + \frac{k_{\beta}}{m_{\beta}} \frac{T_{E}}{L_{\beta}} \sigma_{\beta}^{L}(r,g(r)) \frac{1}{R_{\beta}(r,g(r))}$$
(17b)

with,

$$\frac{1}{R_{\beta}(r,g(r))} = \hat{K}_{\beta}(r,g(r))$$
(18b)

After some simplifications, Eq. (18b) becomes:

$$\widehat{K}_{\beta}\left(r,g\left(r\right)\right) = \widehat{K}_{\beta} = \frac{2r_{\alpha}\sin\theta_{\beta}^{L}}{\left(r_{\alpha}+r_{\beta}\right)^{2}-r_{\alpha}^{2}} = const.$$
(19b)

Additional simplifications are as follows:

$$\sigma_{\alpha}^{L}(r,g(r)) = \sigma_{\alpha}^{L} = const.,$$

and $\sigma_{\beta}^{L}(r,g(r)) = \sigma_{\beta}^{L} = const.$ (20b)

$$\frac{1}{m_{\alpha}} \frac{T_E}{L_{\alpha}} \sigma_{\alpha}^L = M_{\alpha}, \text{ and } \frac{1}{m_{\beta}} \frac{T_E}{L_{\beta}} \sigma_{\beta}^L = M_{\beta}$$
(21b)

Insertion of the above simplifications into Eq. (13) leads to:

$$P_{D}^{R} = \frac{2\pi\nu}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} \right)_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) r dr + \left(N_{E}^{L} - N_{E}^{\beta} \right)_{0}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) r dr + \left(N_{E}^{L} - N_{E}^{\beta} \right)_{s_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) r dr + \left(k_{\alpha} M_{\alpha} \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}} \int_{0}^{r_{\alpha}} \delta N^{L}(r, g(r)) r dr + k_{\beta} M_{\beta} \frac{2r_{\alpha} \sin\theta_{\beta}^{L}}{(r_{\alpha} + r_{\beta})^{2} - r_{\alpha}^{2}} \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, g(r)) r dr + \left(\frac{2\pi\nu}{2D} \left[\int_{0}^{r_{\alpha}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr + \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr + \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr + \left(\frac{2\pi\nu}{2D} \left[\int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr + \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, g(r)) \right]^{2} r dr \right] \right]$$

$$(22b)$$

 a) effect of the solute concentration inhomogeneity on the lamellar structure formation The integral,

$$P_{D}^{L} = \frac{v}{D} \begin{bmatrix} \left(N_{E}^{L} - N_{E}^{\alpha}\right)^{S_{\alpha}} \delta N^{L}\left(x, g\left(x\right)\right) dx + \\ \left(N_{E}^{L} - N_{E}^{\beta}\right)^{S_{\alpha} + S_{\beta}} \delta N^{L}\left(x, g\left(x\right)\right) dx \end{bmatrix} - \\ \frac{v}{D} \begin{bmatrix} k_{\alpha} \int_{0}^{S_{\alpha}} \left[\delta N^{L}\left(x, g\left(x\right)\right) \right]^{2} dx + \\ k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} \int_{0}^{S_{\alpha}} \delta N^{L}\left(x, g\left(x\right)\right) dx + \\ k_{\beta} \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L}\left(x, g\left(x\right)\right) \right]^{2} dx + \\ k_{\beta} A_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}} \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \delta N^{L}\left(x, g\left(x\right)\right) dx \end{bmatrix} + \\ \frac{v}{2D} \begin{bmatrix} \int_{0}^{S_{\alpha}} \left[\delta N^{L}\left(x, g\left(x\right)\right) \right]^{2} dx + \\ \int_{S_{\alpha} + S_{\beta}}^{S_{\alpha}} \left[\delta N^{L}\left(x, g\left(x\right)\right) \right]^{2} dx + \\ \end{bmatrix}$$
(22a)

contains the $\delta N^L(x, g(x))$ – unknown, only.

The $\delta N^L(x, g(x))$ – analytical solution to the diffusion equation is unknown, but the $\delta N^L(x, 0)$ – solution for the plane s/l interface has already been delivered, [2]. However, this discrepancy can be eliminated by introducing the g_S – coefficient of the interplay between the s/l interface curvature and the idealized field of the solute concentration, $\delta N^L(x, 0)$, $S = \alpha, \beta$. Thus, the following definition of the coefficient is proposed:

$$\delta N^{L}(x,g(x)) = \delta N^{L}(x,0) + g_{S}(x,g(x))\hat{K}(x,g(x))$$
(23a)

The definition, Eq. (23a), can be simplified with the use of Eq. (16a), and Eq. (19a), respectively. Moreover, the $g_S(x,g(x))$ – coefficient can be assumed as a parameter which expresses the average interplay, g_S , $S = \alpha, \beta$. Then, Eq. (23a) reduces,

A) for the α – phase lamella

$$\delta N^{L}(x,g(x)) = \delta N^{L}(x,0) + g_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}}$$
(24a)

B) for the β – phase lamella

$$\delta N^{L}(x,g(x)) = \delta N^{L}(x,0) + g_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}}$$
(25a)



Then, Eq. (22a) becomes

$$P_{D}^{L} = \frac{v}{D} \Biggl[\Biggl(N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} \Biggr) + \Biggl(\int_{0}^{S_{\alpha}} \delta N^{L} (x, 0) dx + \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} \int_{0}^{S_{\alpha}} dx \Biggr) + \Biggl(N_{E}^{L} - N_{E}^{\beta} - k_{\beta} A_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}} \Biggr) + \Biggl(\frac{1}{2} - k_{\alpha} \Biggr) \Biggl(\int_{0}^{S_{\alpha} + S_{\beta}} \delta N^{L} (x, 0) dx + \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} dx \Biggr) + \Biggl(\frac{1}{2} - k_{\alpha} \Biggr) \Biggl(\int_{0}^{S_{\alpha}} \left[\delta N^{L} (x, 0) \right]^{2} dx + \frac{2g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}^{2}} \int_{0}^{S_{\alpha}} dx \Biggr) + \Biggr(\frac{1}{2} - k_{\beta} \Biggr) \Biggl(\int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L} (x, 0) \right]^{2} dx + \frac{2g_{\beta} \sin \theta_{\beta}^{L}}{S_{\alpha}^{2}} \int_{0}^{S_{\alpha}} dx \Biggr) + \Biggr(\frac{1}{2} - k_{\beta} \Biggr) \Biggl(\int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L} (x, 0) \right]^{2} dx + \frac{2g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} \Biggr) \Biggr) \Biggr(26a \Biggr) \Biggr) \Biggr(26a \Biggr)$$

After some rearrangements,

$$P_{D}^{L} = \frac{v}{D} \left[\left(N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} + \right) \int_{0}^{S_{\alpha}} \delta N^{L}(x,0) dx + \left(\frac{1}{2} - k_{\alpha} \right) \frac{2 g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{2 g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{2 g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\alpha} \right) \frac{2 g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\alpha} \right) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} + \left(\frac{1}{2} - k_{\alpha} \right) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\alpha} \right) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\alpha} \right) \int_{0}^{S_{\alpha}} \left[\delta N^{L}(x,0) \right]^{2} dx + \left(\frac{1}{2} - k_{\beta} \right) \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L}(x,0) \right]^{2} dx + \left(\frac{1}{2} - k_{\beta} \right) \int_{S_{\alpha}}^{S_{\alpha} + S_{\beta}} \left[\delta N^{L}(x,0) \right]^{2} dx \right]$$

$$(27a)$$

The integration over the *x* – variable, Eq. (27a), is now possible, since the $\delta N^L(x, 0)$ – solution is known, [2]. Thus,

$$\int_{0}^{S_{\alpha}} \delta N^{L}(x,0) dx = \frac{2(S_{\alpha} + S_{\beta})^{2} v N_{0} P^{*}}{D}$$
(28a)

$$\int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \delta N^{L}(x,0) dx = -\frac{2\left(S_{\alpha}+S_{\beta}\right)^{2} v N_{0} P^{*}}{D}$$
(29a)

$$\delta N^{L}(x,g(x)) = \delta N^{L}(x,0) + g_{S}(x,g(x))\hat{K}(x,g(x))$$
(30a)

and,

$$\int_{0}^{S_{\alpha}} \left[\delta N^{L}(x,0) \right]^{2} dx =$$

$$\frac{4 \left(S_{\alpha} + S_{\beta} \right)^{3} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\alpha} \Theta + \frac{R^{*}}{2} \right]$$
(31a)

$$\frac{\int_{S_{\alpha}}^{S_{\alpha}+S_{\beta}} \left[\delta N^{L}(x,0)\right]^{2} dx =}{\frac{4\left(S_{\alpha}+S_{\beta}\right)^{3} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\beta} \Theta - \frac{R^{*}}{2}\right]}$$
(32a)

$$\Theta = \sum_{n=1}^{\infty} \left(\frac{1}{n\pi}\right)^4 \sin^2\left(\frac{n\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right)$$
(33a)

$$R^{*} = \sum_{n=2}^{\infty} \sum_{k=1}^{n-1} \left(\frac{1}{n}\right)^{2} \left(\frac{1}{k}\right)^{2} \left(\frac{1}{\pi}\right)^{5} \sin\left(\frac{n\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right) \sin\left(\frac{k\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right) \\ \left[\frac{1}{n+k} \sin\left(\frac{(n+k)\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right) + \frac{1}{n-k} \sin\left(\frac{(n-k)\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right)\right] + \frac{1}{2} \sum_{n=1}^{\infty} \left(\frac{1}{n\pi}\right)^{5} \sin^{3}\left(\frac{n\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right) \cos\left(\frac{n\pi S_{\alpha}}{S_{\alpha} + S_{\beta}}\right)$$
(34a)

Using Eq. (28a) – Eq. (34a) to solve the integral, Eq. (27a), leads to:

$$P_{D}^{L} = \frac{v}{D} \begin{bmatrix} \left(N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} + \right) \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{2 g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} \end{bmatrix} \\ \frac{2 \left(S_{\alpha} + S_{\beta}\right)^{2} v N_{0} P^{*}}{D} + \\ \left(N_{E}^{L} - N_{E}^{\beta} - k_{\beta} A_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}} + \left(\frac{1}{2} - k_{\beta}\right) \frac{2 g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} \end{bmatrix} \\ \left(-\frac{2 \left(S_{\alpha} + S_{\beta}\right)^{2} v N_{0} P^{*}}{D}\right) + \tag{35a}$$



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$$\begin{pmatrix} N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} A_{\alpha} \frac{\sin \theta_{\alpha}^{L}}{S_{\alpha}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} \end{pmatrix} \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{S_{\alpha}} + \\ \begin{pmatrix} N_{E}^{L} - N_{E}^{\beta} - k_{\beta} A_{\beta} \frac{\sin \theta_{\beta}^{L}}{S_{\beta}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} \end{pmatrix} \frac{g_{\beta} \sin \theta_{\beta}^{L}}{S_{\beta}} + \\ \begin{pmatrix} \frac{1}{2} - k_{\alpha} \end{pmatrix} \frac{4 \left(S_{\alpha} + S_{\beta}\right)^{3} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\alpha} \Theta + \frac{R^{*}}{2} \right] + \\ \begin{pmatrix} \frac{1}{2} - k_{\beta} \end{pmatrix} \frac{4 \left(S_{\alpha} + S_{\beta}\right)^{3} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\beta} \Theta - \frac{R^{*}}{2} \right] \end{bmatrix}$$
(35a ctn)

Eq. (35a) becomes:

$$P_{D}^{L} = \frac{v}{D} \left[\left(N_{E}^{\beta} - N_{E}^{\alpha} \right) \frac{2 N_{0} P^{*}}{D} \left(S_{\alpha} + S_{\beta} \right)^{2} v + \left\{ \left(N_{E}^{L} - N_{E}^{\alpha} \right) g_{\alpha} \sin \theta_{\alpha}^{L} + \left(N_{E}^{L} - N_{E}^{\beta} \right) g_{\beta} \sin \theta_{\beta}^{L} \right\} + \left\{ \frac{1}{2} \Theta - \left(k_{\alpha} V_{\alpha} + k_{\beta} V_{\beta} \right) \Theta - \left(k_{\alpha} - k_{\beta} \right) \frac{R^{*}}{2} \right\} - \frac{4 N_{0}^{2}}{D^{2}} \left(S_{\alpha} + S_{\beta} \right)^{3} v^{2} + \left\{ \left(\frac{1}{2} - k_{\alpha} \right) \frac{g_{\alpha}^{2} \sin^{2} \theta_{\alpha}^{L}}{V_{\alpha}} + \left(\frac{1}{2} - k_{\beta} \right) \frac{g_{\beta}^{2} \sin^{2} \theta_{\beta}^{L}}{V_{\beta}} - \frac{k_{\alpha} A_{\alpha} g_{\alpha} \sin^{2} \theta_{\alpha}^{L}}{V_{\beta}} + \left\{ \left(1 - 2k_{\alpha} \right) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} - \left(1 - 2k_{\beta} \right) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} + \frac{k_{\beta} A_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} - \frac{k_{\alpha} A_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} \right\} \frac{2 N_{0} P^{*}}{D} \left(S_{\alpha} + S_{\beta} \right) v \quad (36a)$$

since $S_{\alpha} = (S_{\alpha} + S_{\beta})V_{\alpha}$, and $S_{\beta} = (S_{\alpha} + S_{\beta})V_{\beta}$.

 effect of the solute concentration inhomogeneity on the rod-like structure formation The integral,

$$P_D^R = \frac{2\pi\nu}{D} \begin{bmatrix} \left(N_E^L - N_E^{\alpha}\right) \int_{0}^{r_{\alpha}} \delta N^L \left(r, g\left(r\right)\right) r \, dr + \\ \left(N_E^L - N_E^{\beta}\right) \int_{S_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^L \left(r, g\left(r\right)\right) r \, dr \end{bmatrix} - (22b)$$

$$\frac{2\pi\nu}{D} \begin{bmatrix} k_{\alpha} \int_{0}^{r_{\alpha}} \left[\delta N^{L}(r,g(r)) \right]^{2} r \, dr + \\ k_{\alpha} M_{\alpha} \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}} \int_{0}^{r_{\alpha}} \delta N^{L}(r,g(r)) r \, dr + \\ k_{\beta} \int_{r_{\alpha}}^{r_{\alpha}+r_{\beta}} \left[\delta N^{L}(r,g(r)) \right]^{2} r \, dr + \\ k_{\beta} M_{\beta} \frac{2r_{\alpha}\sin\theta_{\beta}^{L}}{\left(r_{\alpha}+r_{\beta}\right)^{2}-r_{\alpha}^{2}} \int_{r_{\alpha}}^{r_{\alpha}+r_{\beta}} \delta N^{L}(r,g(r)) r \, dr \end{bmatrix}^{+} \\ \frac{2\pi\nu}{2D} \begin{bmatrix} \int_{0}^{r_{\alpha}} \left[\delta N^{L}(r,g(r)) \right]^{2} r \, dr + \\ \int_{r_{\alpha}+r_{\beta}}^{r_{\alpha}} \left[\delta N^{L}(r,g(r)) \right]^{2} r \, dr \end{bmatrix}$$
(22b ctn)

contains the $\delta N^L(r, g(r))$ – unknown, only.

The $\delta N^L(r, g(r))$ – analytical solution to the diffusion equation is unknown, but the $\delta N^L(r, 0)$ – solution for the plane s/l interface has already been delivered, [2]. However, this discrepancy can be eliminated by introducing the g_S – coefficient of the interplay between the s/l interface curvature and the idealized field of the solute concentration, $\delta N^L(r, 0)$, $S = \alpha, \beta$. Thus, the following definition of the coefficient is proposed:

$$\delta N^{L}(r,g(r)) =$$

$$\delta N^{L}(r,0) + g_{S}(r,g(r))\hat{K}(r,g(r))$$
(23b)

The definition, Eq. (23b), can be simplified with the use of Eq. (16b), and Eq. (19b), respectively. Moreover, the $g_S(r, g(r))$ – coefficient can be assumed as a parameter which expresses the average interplay, g_S , $S = \alpha$, β . Then, Eq. (23b) reduces,

A) for the α – phase rod

$$\delta N^{L}(r,g(r)) = \delta N^{L}(r,0) + g_{\alpha} \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}}$$
(24b)

B) for the β – phase matrix

$$\delta N^{L}(r,g(r)) = \delta N^{L}(r,0) + g_{\beta} \frac{2r_{\alpha}\sin\theta_{\beta}^{L}}{\left(r_{\alpha}+r_{\beta}\right)^{2}-r_{\alpha}^{2}} \quad (25b)$$

Then, Eq. (22b) becomes,

$$P_D^R = \frac{2\pi\nu}{D} \left[\begin{pmatrix} N_E^L - N_E^\alpha - k_\alpha M_\alpha \frac{2\sin\theta_\alpha^L}{r_\alpha} + \\ \left(\frac{1}{2} - k_\alpha\right) \frac{4g_\alpha \sin\theta_\alpha^L}{r_\alpha} \end{pmatrix} \right]$$
$$\int_0^{r_\alpha} \delta N^L(r,0)r \, dr +$$
(27b)

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$$\begin{cases} N_{E}^{L} - N_{E}^{\beta} - k_{\beta} M_{\beta} \frac{2r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{4g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} \\ \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \delta N^{L}(r, 0) r dr + \\ \left(\frac{N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} M_{\alpha} \frac{2 \sin \theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{2g_{\alpha} \sin \theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{2g_{\alpha} \sin \theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{2g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{2g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \frac{2g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \int_{0}^{r_{\alpha}} \left[\delta N^{L}(r, 0)\right]^{2} r dr + \\ \left(\frac{1}{2} - k_{\beta}\right) \int_{0}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, 0)\right]^{2} r dr + \\ \left(\frac{1}{2} - k_{\beta}\right) \int_{r_{\alpha}}^{r_{\alpha} + r_{\beta}} \left[\delta N^{L}(r, 0)\right]^{2} r dr \end{bmatrix}$$
(27b ctn)

The integration over the r – variable, Eq. (27b), is now possible, since the $\delta N^L(r, 0)$ – solution is known, [2]. Thus,

$$\int_{0}^{r_{\alpha}} \delta N^{L}(r,0) r \, dr = \frac{2(r_{\alpha} + r_{\beta})^{3} V_{\alpha} v N_{0} E}{D}$$
(28b)

$$\int_{r_{\alpha}}^{r_{\alpha}+r_{\beta}} \delta N^{L}(r,0)r \ dr = -\frac{2(r_{\alpha}+r_{\beta})^{3}V_{\alpha}vN_{0}E}{D}$$
(29b)

$$E = \sum_{n=1}^{\infty} \frac{J_1^2 \left(\frac{\gamma_n r_\alpha}{r_\alpha + r_\beta}\right)}{\gamma_n^3 J_0^2 (\gamma_n)}$$
(30b)

where γ_n is a root of $J_1(r) = 0$, and is approximately equal to $n\pi$,

$$\frac{\int_{0}^{r_{\alpha}} \left[\delta N^{L}(r,0) \right]^{2} r \, dr =}{\frac{2(r_{\alpha}+r_{\beta})^{4} V_{\alpha} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\alpha} U + 4\sqrt{V_{\alpha}} G^{*} \right]}$$
(31b)

$$\frac{\int_{r_{\alpha}}^{r_{\alpha}+r_{\beta}} \left[\delta N^{L}(r,0)\right]^{2} r \, dr =}{\frac{2\left(r_{\alpha}+r_{\beta}\right)^{4} V_{\alpha} v^{2} N_{0}^{2}}{D^{2}} \left[S^{*}-V_{\alpha} U-4\sqrt{V_{\alpha}} G^{*}\right]} \quad (32b)$$

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$$S^{*} = \sum_{n=1}^{\infty} \frac{J_{1}^{2} \left(\frac{\gamma_{n} r_{\alpha}}{r_{\alpha} + r_{\beta}} \right)}{\gamma_{n}^{4} J_{0}^{2} (\gamma_{n})}$$
(33b)

.

$$U = \sum_{n=1}^{\infty} \frac{J_1^2 \left(\frac{\gamma_n r_\alpha}{r_\alpha + r_\beta}\right)}{\gamma_n^4 J_0^4 (\gamma_n)} \left[J_1^2 \left(\frac{\gamma_n r_\alpha}{r_\alpha + r_\beta}\right) \right] + J_0^2 \left(\frac{\gamma_n r_\alpha}{r_\alpha + r_\beta}\right)$$
(34b)

$$G^{*} = \sum_{n=2}^{\infty} \sum_{k=1}^{n-1} \frac{J_{1}\left(\frac{\gamma_{n} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right) J_{1}\left(\frac{\gamma_{k} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right)}{\gamma_{n}^{2} J_{0}^{2}(\gamma_{n}) \gamma_{k}^{2} J_{0}^{2}(\gamma_{k})}$$

$$\left[\frac{\frac{\gamma_{n} J_{0}\left(\frac{\gamma_{k} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right) J_{1}\left(\frac{\gamma_{n} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right)}{\gamma_{n}^{2} - \gamma_{k}^{2}} - \frac{\gamma_{k} J_{0}\left(\frac{\gamma_{n} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right) J_{1}\left(\frac{\gamma_{k} r_{\alpha}}{r_{\alpha} + r_{\beta}}\right)}{\gamma_{n}^{2} - \gamma_{k}^{2}}\right]$$
(34b')

Using Eq. (28b) – Eq. (34b') to solve the integral, Eq. (27b), leads to:

$$P_{D}^{R} = \frac{2\pi v}{D} \left[\begin{pmatrix} N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} M_{\alpha} \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{4g_{\alpha} \sin\theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\beta}\right)^{3} V_{\alpha} v N_{0} E \\ D + \\ \begin{pmatrix} N_{E}^{L} - N_{E}^{\beta} - k_{\beta} M_{\beta} \frac{2r_{\alpha} \sin\theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{4g_{\beta} r_{\alpha} \sin\theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} \right) \left(-\frac{2\left(r_{\alpha} + r_{\beta}\right)^{3} V_{\alpha} v N_{0} E}{D} \right) + \\ \begin{pmatrix} N_{E}^{L} - N_{E}^{\alpha} - k_{\alpha} M_{\alpha} \frac{2\sin\theta_{\alpha}^{L}}{r_{\alpha}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{2g_{\alpha} \sin\theta_{\alpha}^{L}}{r_{\alpha}} + \\ \end{pmatrix} \frac{2g_{\alpha} \sin\theta_{\alpha}^{L}}{r_{\alpha}} \frac{r_{\alpha}^{2}}{2} + \quad (35b)$$

)





$$\begin{pmatrix} N_{E}^{L} - N_{E}^{\beta} - k_{\beta} M_{\beta} \frac{2r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{2g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} \end{pmatrix}^{2} \\ \frac{2g_{\beta} r_{\alpha} \sin \theta_{\beta}^{L}}{\left(r_{\alpha} + r_{\beta}\right)^{2} - r_{\alpha}^{2}} + \\ \left(\frac{1}{2} - k_{\alpha}\right) \frac{2\left(r_{\alpha} + r_{\beta}\right)^{4} V_{\alpha} v^{2} N_{0}^{2}}{D^{2}} \left[V_{\alpha} U + 4\sqrt{V_{\alpha}} G^{*}\right] + \\ \left(\frac{1}{2} - k_{\beta}\right) \frac{2\left(r_{\alpha} + r_{\beta}\right)^{4} V_{\alpha} v^{2} N_{0}^{2}}{D^{2}} \left[S^{*} - V_{\alpha} U - 4\sqrt{V_{\alpha}} G^{*}\right] \right]$$

$$(35b)$$

Eq. (35b) becomes,

$$P_{D}^{R} = \frac{2 \pi v}{D} \left[\left(N_{E}^{\beta} - N_{E}^{\alpha} \right) \frac{2 V_{\alpha} N_{0} E}{D} \left(r_{\alpha} + r_{\beta} \right)^{3} v + \left\{ \left(N_{E}^{L} - N_{E}^{\alpha} \right) g_{\alpha} \sin \theta_{\beta}^{L} + \left(N_{E}^{L} - N_{E}^{\beta} \right) g_{\beta} \sin \theta_{\beta}^{L} \right\} \right\} \cdot \left\{ \left(N_{E}^{L} - N_{E}^{\alpha} \right) g_{\alpha} \sin \theta_{\beta}^{L} + \left\{ \frac{1}{2} S^{*} - k_{\beta} S^{*} - \left(k_{\alpha} - k_{\beta} \right) \right\} \right\} \cdot \frac{2 V_{\alpha} N_{0}^{2}}{D^{2}} \left(r_{\alpha} + r_{\beta} \right)^{4} v^{2} + \left\{ \left(1 - 2 k_{\alpha} \right) g_{\alpha}^{2} \sin^{2} \theta_{\beta}^{L} + \left(1 - 2 k_{\beta} \right) g_{\beta}^{2} \sin^{2} \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} - 2 k_{\alpha} M_{\alpha} g_{\alpha} \sin^{2} \theta_{\alpha}^{L} - 2 k_{\beta} M_{\beta} g_{\beta} \sin^{2} \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} \right\} + \left\{ 4 \left(1 - 2 k_{\alpha} \right) g_{\alpha} \sin \theta_{\beta}^{L} + 4 \left(1 - 2 k_{\beta} \right) g_{\beta} \sin \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} - 4 k_{\alpha} M_{\alpha} \sin \theta_{\alpha}^{L} - 4 k_{\beta} M_{\beta} \sin \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} \right\} \cdot \left\{ \frac{\sqrt{V_{\alpha}} N_{0} E}{D} \left(r_{\alpha} + r_{\beta} \right)^{2} v \right\}$$
(36b)

since $r_{\alpha} = (r_{\alpha} + r_{\beta}) \sqrt{V_{\alpha}}$.

3. Growth Law for the regular structure formation

According to the thermodynamics of irreversible processes, the stationary state is defined by the criterion of minimum entropy production, [4]. Thus, the application of this criterion allows for defining the size of the regular eutectic structure.

The eutectic transformation proceeds under the stationary state in such a way that the regular lamellae / rods, growing at an imposed thermal gradient and a constant solidification

rate, evince inter-phase spacing (λ, R) which corresponds to the minimum entropy production.

Therefore, the mathematical optimization of the regular morphology formation described by the entropy production leads to the formulation of the Growth Law for lamellar or rod-like structure, respectively.

for lamellar eutectic structure formation a) Eq. (36a) can be rewritten as follows:

$$P_{D}^{L}(v,\lambda) = W_{1}v + W_{2}\frac{v}{S_{\alpha} + S_{\beta}} + W_{3}v^{2}(S_{\alpha} + S_{\beta}) + W_{4}v^{2}(S_{\alpha} + S_{\beta})^{2} + W_{5}v^{3}(S_{\alpha} + S_{\beta})^{3}$$
(37a)

$$W_1 = \left(N_E^L - N_E^\alpha\right) \frac{g_\alpha}{D} \sin \theta_\alpha^L + \left(N_E^L - N_E^\beta\right) \frac{g_\beta}{D} \sin \theta_\beta^L \quad (38a)$$

$$W_{2} = \left(\frac{1}{2} - k_{\alpha}\right) \frac{g_{\alpha}^{2} \sin^{2} \theta_{\alpha}^{L}}{DV_{\alpha}} + \left(\frac{1}{2} - k_{\beta}\right) \frac{g_{\beta}^{2} \sin^{2} \theta_{\beta}^{L}}{DV_{\beta}} - \frac{k_{\alpha} A_{\alpha} g_{\alpha} \sin^{2} \theta_{\alpha}^{L}}{DV_{\alpha}} - \frac{k_{\beta} A_{\beta} g_{\beta} \sin^{2} \theta_{\beta}^{L}}{DV_{\beta}}$$
(39a)

$$W_{3} = \begin{cases} (1 - 2k_{\alpha}) \frac{g_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} - \\ (1 - 2k_{\beta}) \frac{g_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} - \\ \frac{k_{\alpha} A_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} + \frac{k_{\beta} A_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} \end{cases} \frac{2N_{0} P^{*}}{D^{2}} \quad (40a)$$

$$W_{4} = \left(N_{E}^{\beta} - N_{E}^{\alpha}\right) \frac{2N_{0}P^{*}}{D^{2}}$$
(41a)

$$W_{5} = \begin{cases} \frac{1}{2} \Theta - \left(k_{\alpha} V_{\alpha} + k_{\beta} V_{\beta}\right) \Theta - \\ \left(k_{\alpha} - k_{\beta}\right) \frac{R^{*}}{2} \end{cases} \begin{cases} \frac{4 N_{0}^{2}}{D^{3}} & (42a) \end{cases}$$

The first derivative is:

$$\frac{\partial P_D^L}{\partial \lambda}\Big|_{\nu} = -W_2 \frac{\nu}{\left(S_{\alpha} + S_{\beta}\right)^2} + W_3 \nu^2 + 2W_4 \nu^2 \left(S_{\alpha} + S_{\beta}\right) + 3W_5 \nu^3 \left(S_{\alpha} + S_{\beta}\right)^2$$
(43a)

Since $\frac{\partial \left(P_D^L\right)}{\partial \lambda}\Big|_{\nu} = 0$, and $\frac{\partial^2 \left(P_D^L\right)}{\partial \lambda^2}\Big|_{\nu} > 0$ are satisfied, there-

fore, the Growth Law is:

$$3W_5 v^2 \left(S_{\alpha} + S_{\beta}\right)^4 + 2W_4 v \left(S_{\alpha} + S_{\beta}\right)^3 + W_3 v \left(S_{\alpha} + S_{\beta}\right)^2 = W_2 \qquad (44a)$$



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b) for rod-like eutectic structure formation Eq. (36b) can be rewritten as follows:

$$P_{D}^{R}(v,R) = V_{1}v(r_{\alpha} + r_{\beta}) + V_{2}v + V_{3}v^{2}(r_{\alpha} + r_{\beta})^{2} + V_{4}v^{2}(r_{\alpha} + r_{\beta})^{3} + V_{5}v^{3}(r_{\alpha} + r_{\beta})^{4}$$
(37b)

$$V_{1} = \begin{cases} \left(N_{E}^{L} - N_{E}^{\alpha}\right)g_{\alpha}\sin\theta_{\alpha}^{L} + \\ \left(N_{E}^{L} - N_{E}^{\beta}\right)g_{\beta}\sin\theta_{\beta}^{L} \end{cases} \frac{2\pi\sqrt{V_{\alpha}}}{D}$$
(38b)

$$V_{2} = \left\{ \left(1 - 2k_{\alpha}\right)g_{\alpha}^{2}\sin^{2}\theta_{\alpha}^{L} + \left(1 - 2k_{\beta}\right)g_{\beta}^{2}\sin^{2}\theta_{\beta}^{L}\frac{V_{\alpha}}{V_{\beta}} - 2k_{\alpha}M_{\alpha}g_{\alpha}\sin^{2}\theta_{\alpha}^{L} - 2k_{\beta}M_{\beta}g_{\beta}\sin^{2}\theta_{\beta}^{L}\frac{V_{\alpha}}{V_{\beta}} \right\} \frac{2\pi}{D}$$
(39b)

$$V_{3} = \left\{ 4 \left(1 - 2k_{\alpha} \right) g_{\alpha} \sin \theta_{\alpha}^{L} + 4 \left(1 - 2k_{\beta} \right) g_{\beta} \sin \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} - 4k_{\alpha} M_{\alpha} \sin \theta_{\alpha}^{L} - 4k_{\beta} M_{\beta} \sin \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} \right\} \frac{2\pi \sqrt{V_{\alpha}} N_{0} E}{D^{2}}$$
(40b)

$$V_4 = \left(N_E^\beta - N_E^\alpha\right) \frac{4\pi V_\alpha N_0 E}{D^2} \tag{41b}$$

$$V_{5} = \begin{cases} \frac{1}{2}S^{*} - k_{\beta}S^{*} - (k_{\alpha} - k_{\beta}) \\ (V_{\alpha}U + 4\sqrt{V_{\alpha}}G^{*}) \end{cases} \frac{4\pi V_{\alpha}N_{0}^{2}}{D^{3}} \qquad (42b)$$

The first derivative is:

$$\frac{\partial \left(P_D^R\right)}{\partial R}\Big|_{\nu} = V_1 \nu + 2V_3 \nu^2 \left(r_{\alpha} + r_{\beta}\right) + 3V_4 \nu^2 \left(r_{\alpha} + r_{\beta}\right)^2 + 4V_5 \nu^3 \left(r_{\alpha} + r_{\beta}\right)^3$$
(43b)

Since
$$\frac{\partial \left(P_D^R\right)}{\partial R}\Big|_{\nu} = 0$$
, and $\frac{\partial^2 \left(P_D^R\right)}{\partial R^2}\Big|_{\nu} > 0$ are satisfied, there-

fore, the Growth Law is:

$$4V_{5}v^{2}(r_{\alpha}+r_{\beta})^{3}+3V_{4}v(r_{\alpha}+r_{\beta})^{2}+$$

$$2V_{3}v(r_{\alpha}+r_{\beta})=-V_{1}$$
 (44b)

500 μm

cording to the Growth Law, Eq. (44), the regular eutectic structure evinces one and only one spacing, $\lambda = 2(S_{\alpha} + S_{\beta})$, or $R = r_{\alpha} + r_{\beta}$, Fig. 3, respectively, when the v – growth rate is constant and solidification proceeds at minimum entropy production.

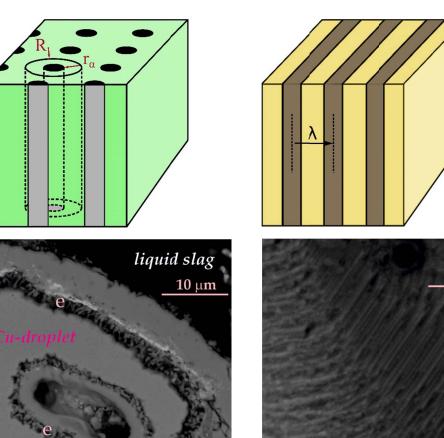


Fig. 3. Spacing in the regular structure, a) rod-like eutectic, b) lamellar eutectic, and its confirmation in the real morphology (industry condition), c) rod-like $Cu-Cu_2O$ – eutectic (e – area) located at the envelopes of the coagulated Cu – droplets, d) lamellar $Cu-Cu_2O$ – eutectic structure

20.0kV 4.7mm x11.0k BSE

4. Effect of the s/l interface curvature onto the solute concentration field

Description of the solute concentration field provided for the plane s/l interface, $\delta N^L(x, 0)$, and $\delta N^L(r, 0)$, respectively, [2], has been used in the current calculation of the entropy production. Thereby, the g_S – coefficient of the interplay between this ideal field of the solute concentration and s/l interface curvature, Eq. (23), is introduced to reproduce, even in an approximate way, the $\delta N^L(x, g(x))$ -, and $\delta N^L(r, g(r))$ – real field of the solute concentration required by the studied integral.

The g_S – coefficient depends on the s/l interface curvature which varies with the v – growth rate. Three examples of the varying s/l interface curvature are shown schematically in Fig. 4. The interphase spacing, λ , or R, Fig. 3, also depends on the growth rate, Eq. (43). Moreover, the crystallographic orientation of both eutectic phases changes with the varying growth rate. Consequentially, the specific surface free energies (vectors in Fig. 4) are modified to satisfy the vectors' parallelogram which constitutes the mechanical equilibrium at the triple point of the s/l interface.

Finally, the rotation of the mentioned vectors is observed in the function of growth rate imposed on the *Bridgman's* system. As the crystallographic orientation varies with growth rate and the resulting mechanical equilibrium is subjected to proper modifications, the influence of the anisotropy of the specific surface free energies upon the entropy production becomes obvious (W_j , and V_j – coefficients, j = 1, ..., 5, Eq. (38) – Eq. (42), contain some capillary parameters which form the mechanical equilibrium, Fig. 4).

It is assumed that the A_S -, and M_S - term, Eq. (21) (which comes from Eq. (14), and Eq. (17), respectively) have the same meaning as the g_S - coefficients, $S = \alpha, \beta$. Thus,

a) for the lamellar structure formation

$$\frac{1}{m_{\alpha}} \frac{T_E}{L_{\alpha}} \sigma_{\alpha}^L = A_{\alpha} \equiv g_{\alpha}$$
(45a)

$$\frac{1}{m_{\beta}} \frac{T_E}{L_{\beta}} \sigma_{\beta}^L = A_{\beta} \equiv g_{\beta}$$
(46a)

b) for the rod-like structure formation

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$$\frac{1}{n_{\alpha}} \frac{T_E}{L_{\alpha}} \sigma_{\alpha}^L = M_{\alpha} \equiv g_{\alpha}$$
(45b)

$$\frac{1}{m_{\beta}} \frac{T_E}{L_{\beta}} \sigma_{\beta}^L = M_{\beta} \equiv g_{\beta}$$
(46b)

The above formulas allow to redefine the material's coefficients in the *Growth Law*, Eq. (44). Thus,

a) for the lamellar structure formation

$$W_{1} = \left(N_{E}^{L} - N_{E}^{\alpha}\right) \frac{A_{\alpha}}{D} \sin \theta_{\alpha}^{L} + \left(N_{E}^{L} - N_{E}^{\beta}\right) \frac{A_{\beta}}{D} \sin \theta_{\beta}^{L}$$
(47a)

$$W_{2} = \left(\frac{1}{2} - 2k_{\alpha}\right) \frac{A_{\alpha}^{2} \sin^{2} \theta_{\alpha}^{L}}{D V_{\alpha}} + \left(\frac{1}{2} - 2k_{\beta}\right) \frac{A_{\beta}^{2} \sin^{2} \theta_{\beta}^{L}}{D V_{\beta}}$$
(48a)

$$W_{3} = \begin{cases} (1 - 3k_{\alpha}) \frac{A_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} - \\ (1 - 3k_{\beta}) \frac{A_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} \end{cases} \frac{2 N_{0} P^{*}}{D^{2}}$$
(49a)

$$W_{4} = \left(N_{E}^{\beta} - N_{E}^{\alpha}\right) \frac{2N_{0}P^{*}}{D^{2}}$$
(50a)

$$W_{5} = \begin{cases} \frac{1}{2} \Theta - \left(k_{\alpha} V_{\alpha} + k_{\beta} V_{\beta}\right) \Theta - \\ \left(k_{\alpha} - k_{\beta}\right) \frac{R^{*}}{2} \end{cases} \begin{cases} \frac{4 N_{0}^{2}}{D^{3}} \end{cases}$$
(51a)

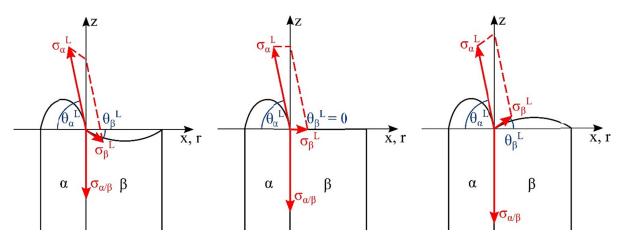


Fig. 4. Mechanical equilibrium (parallelogram of vectors) at the triple point of the s/l interface for: a) convex/concave -, b) convex/plane -, c) convex/convex interface



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b) for the rod-like structure formation

$$V_{1} = \begin{cases} \left(N_{E}^{L} - N_{E}^{\alpha}\right)M_{\alpha}\sin\theta_{\alpha}^{L} + \\ \left(N_{E}^{L} - N_{E}^{\beta}\right)M_{\beta}\sin\theta_{\beta}^{L} \end{cases} \frac{2\pi\sqrt{V_{\alpha}}}{D}$$
(47b)

$$V_{2} = \begin{cases} \left(1 - 4k_{\alpha}\right)M_{\alpha}^{2}\sin^{2}\theta_{\alpha}^{L} + \\ \left(1 - 4k_{\beta}\right)M_{\beta}^{2}\sin^{2}\theta_{\beta}^{L}\frac{V_{\alpha}}{V_{\beta}} \end{cases} \frac{2\pi}{D}$$
(48b)

$$V_{3} = \begin{cases} 4(1-3k_{\alpha})M_{\alpha}\sin\theta_{\alpha}^{L} - \\ 4(1-3k_{\beta})M_{\beta}\sin\theta_{\beta}^{L}\frac{V_{\alpha}}{V_{\beta}} \end{cases} \frac{2\pi\sqrt{V_{\alpha}}N_{0}E}{D^{2}} \quad (49b) \end{cases}$$

$$V_{4} = \left(N_{E}^{\beta} - N_{E}^{\alpha}\right) \frac{4\pi V_{\alpha} N_{0} E}{D^{2}}$$
(50b)

$$\overline{P}_{D}^{R}(v,R) = \overline{V}_{1} \frac{v}{\left(r_{\alpha} + r_{\beta}\right)} + \overline{V}_{2} \frac{v}{\left(r_{\alpha} + r_{\beta}\right)^{2}} + \overline{V}_{3} v^{2} + \overline{V}_{4} v^{2} \left(r_{\alpha} + r_{\beta}\right) + \overline{V}_{5} v^{3} \left(r_{\alpha} + r_{\beta}\right)^{2}$$
(51b)

5. Average entropy production per unit time

Generally, the average entropy production per unite time is defined by Eq. (3). This mode of the mathematical treatment applied to Eq. (37),

a) for the lamellar structure formation

$$P_{D}^{L}(v,\lambda) = W_{1}v + W_{2}\frac{v}{S_{\alpha} + S_{\beta}} + W_{3}v^{2}(S_{\alpha} + S_{\beta}) + W_{4}v^{2}(S_{\alpha} + S_{\beta})^{2} + W_{5}v^{3}(S_{\alpha} + S_{\beta})^{3}$$
(37a)

leads to the formulation of the following relationship:

$$\overline{P}_{D}^{L}(v,\lambda) = \overline{W}_{1} \frac{v}{\left(S_{\alpha} + S_{\beta}\right)} + \overline{W}_{2} \frac{v}{\left(S_{\alpha} + S_{\beta}\right)^{2}} + \overline{W}_{3} v^{2} + \overline{W}_{4} v^{2} \left(S_{\alpha} + S_{\beta}\right) + \overline{W}_{5} v^{3} \left(S_{\alpha} + S_{\beta}\right)^{2}$$
(52a)

$$\overline{W}_{1} = \left(N_{E}^{L} - N_{E}^{\alpha}\right) \frac{A_{\alpha}}{D} \sin \theta_{\alpha}^{L} + \left(N_{E}^{L} - N_{E}^{\beta}\right) \frac{A_{\beta}}{D} \sin \theta_{\beta}^{L} \quad (53a)$$

$$\overline{W}_{2} = \left(\frac{1}{2} - 2k_{\alpha}\right) \frac{A_{\alpha}^{2} \sin^{2} \theta_{\alpha}^{L}}{D V_{\alpha}} + \left(\frac{1}{2} - 2k_{\beta}\right) \frac{A_{\beta}^{2} \sin^{2} \theta_{\beta}^{L}}{D V_{\beta}}$$
(54a)

$$\overline{W}_{3} = \left\{ \left(1 - 3k_{\alpha}\right) \frac{A_{\alpha} \sin \theta_{\alpha}^{L}}{V_{\alpha}} - \left(1 - 3k_{\beta}\right) \frac{A_{\beta} \sin \theta_{\beta}^{L}}{V_{\beta}} \right\} \frac{2N_{0}P^{*}}{D^{2}}$$
(55a)
$$\overline{W}_{4} = \left(N_{E}^{\beta} - N_{E}^{\alpha}\right) \frac{2N_{0}P^{*}}{D^{2}}$$
(56a)

$$\overline{W}_{5} = \left\{\frac{1}{2}\Theta - \left(k_{\alpha}V_{\alpha} + k_{\beta}V_{\beta}\right)\Theta - \left(k_{\alpha} - k_{\beta}\right)\frac{R^{*}}{2}\right\}\frac{4N_{0}^{2}}{D^{3}} \quad (57a)$$

b) for the rod-like structure formation

$$P_{D}^{R}(v,R) = V_{1}v(r_{\alpha}+r_{\beta}) + V_{2}v + V_{3}v^{2}(r_{\alpha}+r_{\beta})^{2} + V_{4}v^{2}(r_{\alpha}+r_{\beta})^{3} + V_{5}v^{3}(r_{\alpha}+r_{\beta})^{4}$$
(37b)

leads to the formulation of the following relationship:

$$\overline{P}_{D}^{R}(v,R) = \overline{V_{1}}\frac{v}{\left(r_{\alpha}+r_{\beta}\right)} + \overline{V_{2}}\frac{v}{\left(r_{\alpha}+r_{\beta}\right)^{2}} + \overline{V_{3}}v^{2} + \overline{V_{4}}v^{2}\left(r_{\alpha}+r_{\beta}\right) + \overline{V_{5}}v^{3}\left(r_{\alpha}+r_{\beta}\right)^{2}$$
(52b)

$$\overline{V}_{1} = \begin{cases} \left(N_{E}^{L} - N_{E}^{\alpha}\right)M_{\alpha}\sin\theta_{\alpha}^{L} + \\ \left(N_{E}^{L} - N_{E}^{\beta}\right)M_{\beta}\sin\theta_{\beta}^{L} \end{cases} \frac{2\sqrt{V_{\alpha}}}{D}$$
(53b)

$$\overline{V}_{2} = \begin{cases} \left(1 - 4k_{\alpha}\right) M_{\alpha}^{2} \sin^{2} \theta_{\alpha}^{L} + \\ \left(1 - 4k_{\beta}\right) M_{\beta}^{2} \sin^{2} \theta_{\beta}^{L} \frac{V_{\alpha}}{V_{\beta}} \end{cases} \frac{2}{D}$$
(54b)

$$\overline{V}_{3} = \begin{cases} 4(1-3k_{\alpha})M_{\alpha}\sin\theta_{\alpha}^{L} - \\ 4(1-3k_{\beta})M_{\beta}\sin\theta_{\beta}^{L}\frac{V_{\alpha}}{V_{\beta}} \end{cases} \frac{2\sqrt{V_{\alpha}}N_{0}E}{D^{2}} \qquad (55b) \end{cases}$$

$$\overline{W}_4 = \left(N_E^\beta - N_E^\alpha\right) \frac{2N_0 P^*}{D^2}$$
(56b)

$$\overline{V}_{5} = \begin{cases} \frac{1}{2}S^{*} - k_{\beta}S^{*} - (k_{\alpha} - k_{\beta}) \\ (V_{\alpha}U + 4\sqrt{V_{\alpha}}G^{*}) \end{cases} \frac{4V_{\alpha}N_{0}^{2}}{D^{3}}$$
(57b)

One could reconsider the derivation / minimization with regard to Eq. (52),

$$\overline{P}_{D}^{L}(\boldsymbol{\nu},\boldsymbol{\lambda}) = \overline{W}_{1} \frac{\boldsymbol{\nu}}{\left(\boldsymbol{S}_{\boldsymbol{\alpha}} + \boldsymbol{S}_{\boldsymbol{\beta}}\right)} + \overline{W}_{2} \frac{\boldsymbol{\nu}}{\left(\boldsymbol{S}_{\boldsymbol{\alpha}} + \boldsymbol{S}_{\boldsymbol{\beta}}\right)^{2}} + \overline{W}_{3} \boldsymbol{\nu}^{2} + \overline{W}_{4} \boldsymbol{\nu}^{2} \left(\boldsymbol{S}_{\boldsymbol{\alpha}} + \boldsymbol{S}_{\boldsymbol{\beta}}\right) + \overline{W}_{5} \boldsymbol{\nu}^{3} \left(\boldsymbol{S}_{\boldsymbol{\alpha}} + \boldsymbol{S}_{\boldsymbol{\beta}}\right)^{2}$$
(52a)

$$\overline{P}_{D}^{R}(v,R) = \overline{V}_{1}\frac{v}{(r_{\alpha}+r_{\beta})} + \overline{V}_{2}\frac{v}{(r_{\alpha}+r_{\beta})^{2}} + \overline{V}_{3}v^{2} + \overline{V}_{4}v^{2}(r_{\alpha}+r_{\beta}) + \overline{V}_{5}v^{3}(r_{\alpha}+r_{\beta})^{2}$$
(52b)

in order to obtain a new modified version of the expression for the *Growth Law* for both analyzed regular eutectics according to the criterion: $\partial \overline{P}_D^L / \partial \lambda |_{\nu} = 0$, or $\partial \overline{P}_D^R / \partial R |_{\nu} = 0$, respectively.



6. Concluding remarks

The current theory proves that morphological transformations observed within the layers strengthening the (Zn) – single crystal have the thermodynamic background. Since the experiment was performed under stationary state, the only criterion which could be used in such a model is the theorem of *minimum entropy production*.

Therefore, entropy production per unit time is calculated for the both morphologies formation and subsequently, subjected to the minimization.

Calculation of the entropy production per unit time, Eq. (2), is currently limited to the entropy production associated with the mass transfer only. It is self-explanatory because heat transfer runs very quickly in comparison with the mass transfer. Thus, contribution of the heat transfer to the entropy production is negligible, [5].

The application of the postulated criterion allows for formulating the *Growth Law* for both eutectic structures appearance, [6], [7].

According to the formulated *Growth Law*, Eq. (44), the regular eutectic structure evinces one and only one spacing, $\lambda = 2(S_{\alpha} + S_{\beta})$, or $R = r_{\alpha} + r_{\beta}$, Fig. 3, respectively, when the v-growth rate is constant and solidification proceeds at minimum entropy production.

However, the newly formulated criterion which says: *in the structural – thermodynamic competition the winner is this kind of the pattern for which minimum entropy production is lower*, is proposed to be verified in the next parts of the current model. Additionally, application of the concept of marginal stability to define the *operating range* for the irregular eutectic structure formation will be shown.

Moreover, descriptions of both irregular – into regular structure transformation (debranching), and regular rod-like -,

- into regular lamellar structure transformation will be delivered. Finally, examination of:
- a) a newly developed theory for the solute micro-field formation with the verification of the local mass balance which allows to display the leading phase protrusion
- a newly developed model for the solute micro-segregation and redistribution will be performed.

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