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# The Criterion of Minimum Entropy Production in Eutectic Growth

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## Abstract

The paper presents adaptation problem of lamellar/rod growth of eutectic. The transformation of eutectic microstructure was investigated systematically. A interpretation of the eutectic growth with theory minimum entropy production was presented.

**Keywords:** Entropy, Minimum entropy production, Eutectic, Lamellar structure, Rod structure

## 1. Introduction

The majority of industrial casting alloys are eutectic or near eutectic in composition. Eutectic microstructures form in alloys when two or more phases grow simultaneously in a co-operative manner. Many eutectic systems exhibit either a lamellar or rod like structure depending on solidification conditions). Especially, growth rate plays a crucial role in the lamella / rod transformation.

In classical physics, the entropy of a physical system is proportional to the quantity of energy no longer available to do physical work. Entropy is central to the second law of thermodynamics, which states that in an isolated system any activity increases the entropy [1]:

In thermodynamics, a physical system is a collection of objects (bodies) whose state is parameterized by several characteristics such as the distribution of density, pressure, temperature, velocity, chemical potential, etc. The change of entropy of a physical system when it passes from one state to another equals:

$$\Delta S = \int \frac{dQ}{T}, \quad (1)$$

where  $dQ$  denotes an element of heat being absorbed (or emitted; then it has negative sign) by a body,  $T$  is the absolute

temperature of that body at that moment, and the integration is over all elements of heat active in the passage. The above formula allows one to compare the entropies of different states of a system, or to compute the entropy of each state up to a constant (which is satisfactory in most cases). The absolute value of entropy is established by the third law of thermodynamics.

Notice that when an element  $dQ$  of heat is transmitted from a warmer body at temperature  $T_1$  to a cooler one at temperature  $T_2$ , then the entropy of the first body changes by  $-dQ/T_1$ , while that of the other rises by  $dQ/T_2$ . Since  $T_2 < T_1$ , the absolute value of the latter fraction is larger and jointly the entropy of the two-body system increases (while the global energy remains the same) [1].

A system is isolated if it does not interact with its surroundings (i.e., is not influenced in any way). In particular, an isolated system does not exchange energy or matter (or even information) with its surroundings. In virtue of the first law of thermodynamics (the conservation of energy principle), an isolated system can pass only between states of the same global energy. The second law of thermodynamics introduces irreversibility of the evolution: an isolated system cannot pass from a state of higher entropy to a state of lower entropy. Equivalently, the second law says that it is impossible to perform a process whose only final effect is the transmission of heat from a cooler medium to a warmer one. Any such

transmission must involve outside work; the elements participating in the work will also change their states and the overall entropy will rise.

The first and second laws of thermodynamics together imply that an isolated system will tend to the state of maximal entropy among all states of the same energy. This state is called the equilibrium state and reaching it is interpreted as the thermodynamical death of the system. The energy distributed in this state is incapable of any further activity [1].

## 2. The minimum entropy production

In 1945 Prigogine proposed a "Theorem of Minimum Entropy Production" which applies only to the linear regime near a stationary thermodynamically non-equilibrium state. The proof offered by Prigogine is open to serious criticism. A critical and unsupportive discussion of Prigogine's proposal is offered by Bertola (2007) [2], Grandy (2008).

Among others, the so-called principle of minimum entropy production rate is certainly the most debated among scientists. The general statement of the minimum entropy production principle reads: „A steady state has the minimum rate of entropy production with respect to other possible states with the same boundary conditions”. In other words, the theorem of minimum entropy production asserts that, under certain assumptions, the global entropy production rate of a given system attains a minimum value when the processes in the system become stationary. As a special case, one finds the equilibrium states, where entropy is maximum and its rate of production becomes zero [2].

To begin consider a system which exchanges mass and energy with its environment. Let  $dS_i$  be the entropy production in the system due to irreversible processes and  $dS_e$  be the entropy flux due to exchanges between the system and environment. The total entropy change in the system is given by:

$$dS = dS_e + dS_i \quad (2)$$

The second law states that  $dS_i \geq 0$ . However if sufficient low entropy flux enters the system then  $dS_e \leq 0$  and it is possible that  $|dS_e| > |dS_i|$  which implies that  $dS < 0$ . If this is the case then the system will be driven away from equilibrium. It is also possible for the system to eventually reach a steady state ( $dS = 0$ ). It is the process which leads to this steady state and the accompanying coherent behaviour which Prigogine, for special cases, has developed a theory for. Central to this theory is the Minimum Entropy Production rule. Let  $P$  - entropy production due to irreversible processes in the system and  $\sigma$  - local entropy production, then:

$$P = \frac{dS_i}{dt} = \int \delta dV \geq 0 \quad (3)$$

where the integral is over the spatial volume of the system [3].

Using Onsager's Reciprocity Relations it is possible to write:

$$\sigma = L_{kl} X_k X_l \quad (4)$$

where  $X_k$  is the thermodynamic force acting on the system and the summation convention over repeated indices is in effect. Substituting for  $\sigma$ , making several assumptions about the forces, and differentiating with respect to time, leads to:

$$\frac{dP}{dt} = \frac{2}{T} \int \frac{\partial \mu_i}{\partial \rho_j} \frac{\partial \rho_i}{\partial t} \frac{\partial \rho_j}{\partial t} dV \quad (5)$$

The quadratic form in the integral can be shown to be positive semi-definite. It is zero at a steady state, hence:

$$\begin{aligned} dP/dt < 0 & \text{ away from steady-state} \\ dP/dt = 0 & \text{ at a steady-state.} \end{aligned}$$

This is the famous minimum entropy production rule which governs the behaviour of dissipative structures in the steady-state. It can be easily shown that this rule guarantees the stability of steady non-equilibrium states [3].

However the derivation of this rule depends on seven assumptions:

- 1) Local Equilibrium Thermodynamics (LET) applies. The system must be well enough behaved that locally (spatially) equilibrium thermodynamics apply.
- 2) The fluxes can be expressed as a linear combination of the flows using Onsager's Reciprocity Relationship.
- 3) The  $L_{ij}$  used in the expansion of the fluxes are time independent.
- 4) The medium is isotropic.
- 5) The boundary conditions imposed on the system are time independent.
- 6) The system is isothermal.
- 7) The system is in mechanical and thermal equilibrium with its environment. Only mass flow occurs across the boundary.

This set of constraints means that the minimum entropy production rule and most of Prigogine's results apply to a very restrictive set of systems. A general far from equilibrium thermodynamics and theory of self-organization does not exist [3].

An important theorem applicable to steady-state solutions in dissipative systems was stated by Ilya Prigogine: the principle of minimum entropy production, which can be represented using the variational principle:

$$\delta \int Q d^3 r = 0, \quad (6)$$

where  $\Theta$  is the entropy production [4].

## 3. Entropy production, dissipation, energy flux and heat transfer

The relationship between entropy production, dissipation and energy flux or heat transfer is often assumed and not clearly established or stated for the situation under investigation. They are not necessarily the same thing. Often in the literature, erroneously, entropy production, dissipation and heat transfer by a system are treated as the same quantity. This because of the relationship  $dS = dQ/T$ . ( $S$  - entropy and  $Q$  - heat). Many people

misuse this relationship to say  $\Delta S = \Delta Q/T$  and thus conclude that  $\Delta S \propto \Delta Q$ .

Thus, incorrectly, they conclude that the entropy change in the system is proportional to the heat transfer, which (both the entropy change and heat transfer) is often referred to as dissipation. It is fair to say this, if and only if, there is only one mode of energy transfer from the system, heat transfer to a single environment (reservoir) which is at a fixed temperature. Entropy production and energy dissipation (i.e. the energy coming out the back end) are only equivalent when you have a single thermal dissipation route. Otherwise they are not equivalent (but obviously related) [3].

#### 4. Thermodynamics of the whole solidification process

The thermodynamics of the whole solidification process involves a calculation of entropy production for the regular structure growth. The regular structure formation at steady-state should be described by the criterion of minimum entropy production. For that reason the entropy production,  $P_D$  was calculated assuming an isothermal solid/liquid interface:

$$P_D = \int \sigma_D dV \quad (7)$$

where the entropy production per unit time and unit volume formulated for constant temperature is as follows:

$$\sigma_D = DR^* \varepsilon (N_i (1 - N_i))^{-1} |\text{grad. } N_i|^2 \quad (8)$$

The entropy production, Eq. (9) was calculated for the mass transport associated with thermo-diffusion only, Glansdorff and Prigogine (1971) [7], since the heat transfer was neglected. Also, it was necessary to introduce the solution to diffusion equation for steady state into the integral given by Eq. (7). Therefore, the solution to diffusion equation developed by Jackson and Hunt (1966) was used in the calculation of total entropy production for the considered structures formation. Finally, an average entropy production associated with the mass transport was calculated:

a/ for lamellar structure formation (regular lamellae within generally irregular morphology):

$$\bar{P}_D^L = W_1 v (S_\alpha + S_\beta)^{-1} + W_2 v (S_\alpha + S_\beta)^{-2} + W_3 v^2 + W_4 v^2 (S_\alpha + S_\beta) + W_5 v^3 (S_\alpha + S_\beta)^2 \quad (9)$$

b/ for rod-like structure formation (regular rods within generally irregular morphology):

$$\bar{P}_D^R = V_1 v (r_\alpha + r_\beta)^{-1} + V_2 v (r_\alpha + r_\beta)^{-2} + V_3 v^2 + V_4 v^2 (r_\alpha + r_\beta) + V_5 v^3 (r_\alpha + r_\beta)^2 \quad (10)$$

$W_i$  and  $V_i$ ,  $i = 1, \dots, 5$  - coefficients contain some material parameters that define both lamellar and rod-like structures formation, respectively, Wolczyński and Billia, (1996).

A minimization of Eqs. (9)-(10) involves:

a/ for the formation of lamellar eutectic structure:

$$\frac{\partial \bar{P}_D^L}{\partial (S_\alpha + S_\beta)} = -W_1 v (S_\alpha + S_\beta)^{-2} - 2W_2 v (S_\alpha + S_\beta)^{-3} + 2W_5 v^3 (S_\alpha + S_\beta) = 0 \quad (11)$$

b/ for the formation of rod-like eutectic structure:

$$\frac{\partial \bar{P}_D^R}{\partial (r_\alpha + r_\beta)} = -V_1 v (r_\alpha + r_\beta)^{-2} - 2V_2 v (r_\alpha + r_\beta)^{-3} + 2V_5 v^3 (r_\alpha + r_\beta)^2 = 0 \quad (12)$$

A model of the evolution of the solid / liquid interface curvature versus the varying growth rate  $v$ , with the resultant equilibrium at the triple point was used in the calculation of the minimum entropy production, Eq. (11,12). The above evolution results in crystallographic orientations evolution and confirms the specific surface free energies anisotropy [5 ,6].

#### 5. A parabola of the entropy production

It is postulated that the maximum destabilization of the solid/liquid interface of the non-faceted phase is observed just when the branching begins. The branches decrease the inter-lamellar spacing (this is required by the diffusion). The diminishing of spacing occurs until minimal distance between lamellae is reached. The minimal distance corresponds to regular structure formation in steady-state according to the criterion of minimum entropy production. The wave of perturbation is created at this destabilized s/l interface. It is assumed that the wavelength of maximum destabilization can be referred to as marginal stability. When a perturbation develops then the local growth rate of the non-faceted phase decreases. Thus, the lamellae appear locally at the same time when rods are formed [5,6].

When a perturbation vanishes then the local growth rate increases and reaches the growth rate proper for regular structure formation, locally. In this area a rod-like structure is the stable form within the operating range. As a consequence of branching, the oscillation of the inter-phase spacing also occurs, Figure 1.

The paraboloid of the entropy production is drawn schematically in the "thermodynamic" coordinate system, that is, in function of two thermodynamic forces. Next, it is assumed (for the simplicity) that the paraboloid does not change its shape when entropy production,  $P$ , is calculated for the crystal growth in function of  $v$ ,  $\lambda$  or  $v$ ,  $R$ . Two trajectories are superposed onto the paraboloid, A - trajectory of local minima of the paraboloid for the regular structure formation, B - trajectory of the marginal stability referred to the maximal destabilization of the s/l

interface. Both trajectories intersect each other (at  $K$  - point) for the critical thermal gradient,  $G_k$ , at which an oscillation disappears and irregular structure is completely transformed into regular eutectic structure.

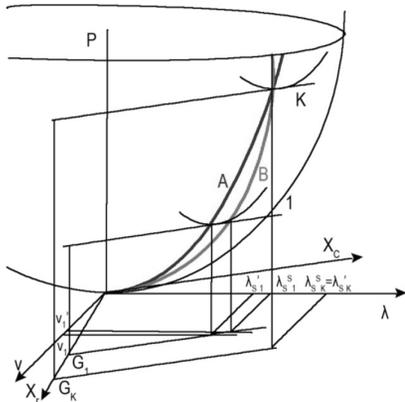


Fig. 1. A paraboloid of the entropy production drawn in function of two thermodynamic forces ( $X_c$ ,  $X_r$ ), with the added so-called “technological” coordinate system ( $v$ ,  $\lambda$ ) [5, 6]

The discussed oscillation can be illustrated on the parabola of entropy production. Such a parabola is to be created by an intersection of the paraboloid (fig. 1), by the plane given for the imposed thermal gradient,  $G$ ,  $v = \text{const}$ , (Prigogine, 1980), as shown in Figure 2.

The oscillation of the inter-phase spacing can be generalized to the oscillation of the whole eutectic system between local minimum of entropy production (an attractor denoted as A) and an adequate state of marginal stability (bifurcation point for branching denoted as B), for a given condition of growth  $v, G = \text{const}$

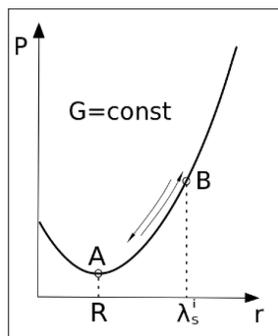


Fig. 2. A parabola of the entropy production for the eutectic rod-like structure formation [5, 6]

It results from the current model (Fig. 2) that, the regular part of the generally irregular eutectic structure is formed at the minimum entropy production localized at the A - parabola minimum which performs the role of attractor for the eutectic system [6].

## 6. Conclusions

The theorem of minimum entropy production is applied to steady and stationary periodic eutectic growth with an oscillating freezing rate. Unsteady eutectic solidification is of practical importance, because solidification rarely occurs at steady state.

The principle of minimum entropy production, which is commonly used to characterise the stationary states of linear dissipative systems obeying Onsager's reciprocity relations, has been reviewed critically. The rigorous analysis of two examples (the heat conduction in a fluid at rest and the combined shear flow and heat conduction in an incompressible fluid) based on the comparison of the theorem's results with those of the field equations of continuum mechanics shows that this theorem cannot be considered as a general variational principle, but at best an approximation method, which converges to the exact solution as the system converges to equilibrium [2].

The theorem proof, as formulated by Prigogine, leads to an erroneous conclusion because the condition of stationary state is not taken into account correctly in the expression of entropy production. When the additional relationship among generalised thermodynamic forces is introduced into the expression of the entropy production, the theorem shows that for systems in a stationary state the entropy production must be zero.

A critical analysis of the theorem proof shows that the minimum entropy production of system in a stationary state cannot be different from zero [2].

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