Physica A 392 (2013) 5757–5763

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Phenomenological model of nonequilibrium solidification

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HIGHLIGHTS

- The maximum entropy production principle is considered as a foundation of nonequilibrium pattern formation.
- Based on the principle, a simple phenomenological model of dendrite growth is developed.
- The model results quantitatively agree with the experimental data.

ARTICLE INFO

Article history:
Received 3 May 2013
Received in revised form 25 June 2013
Available online 25 July 2013

Keywords:
Maximum entropy production principle
Dendrite growth

ABSTRACT

The maximum entropy production principle is used as a foundation for the nonequilibrium solidification theory. Based on this principle, a new simple model of dendrite solidification is proposed. The model predicts the explicit dependency of a dendrite's rate and tip size on supercooling. The obtained results are devoid of the contradictions of the previous models and show quantitative agreement with the recent experimental data for the SCN dendrite.

1. Introduction

Nonequilibrium growth of crystals from different media is typical for many natural and technological processes. Such growth results in the complex, intricate shape of crystals. In terms of appearance, they are divided into dendrites, nonsymmetrical diffusion-limited aggregates (DLA), seaweed-like structures, etc. [1–7]. It is interesting to note here that similar shapes are typical not only for crystal systems but for some biotic systems (e.g. for bacterial colonies) in the process of self-organization (see e.g., Ref. [3]). Currently, most investigations (both theoretical and experimental) deal with the dendrite growth for which a snowflake forming in air supersaturated with water vapor is a typical example. One of the core issues that have been discussed for more than fifty years is the connection between three quantities characterizing the dendrite (see, for example, the reviews [8–13]). These quantities are the dendrite growth rate υ, the dendrite tip size, which is conventionally described by the curvature radius ρ, and the degree of nonequilibrium of the system Δ (a relative quantity of supercooling or supersaturation in the case of crystallization from the melt or from the solution/vapor, respectively). According to the experiments, in the case of preset Δ, the dendrite has certain values of υ and ρ during its growth. The microscope solvability theory[1] is presently the most common method for determining the dependencies $\upsilon(\Delta)$ and $\rho(\Delta)$ [11–14]. This theory analytically studies the growth and stability of a needle crystal by means of the rigorous solution of a heat-conduction problem with the anisotropies of surface energy and kinetic effects. This theory allows predicting the behavior of $\upsilon(\Delta)$ and $\rho(\Delta)$ for a number of the simplest cases of dendrite growth. However, such a method cannot be considered as a basis for material and metallurgical applications because there are no *explicit* dependencies (and fitting formulas) $\upsilon(\Delta)$ and $\rho(\Delta)$ convenient for

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[1] Further referred to as MST for brevity.

0378-4371/$ – see front matter
http://dx.doi.org/10.1016/j.physa.2013.07.037

practical use[2] [13]. At the same time, there is another drawback, in our opinion, the most critical. The dendrite crystallization theory has appeared and been developed as some special problem of mathematical physics[3] intended only for describing dendrite growth.[4] As a result, in a number of cases the selected mathematical method of problem analysis can lead to principally different physical conclusions (for example, in regard to the prerequisites for existence of the stable dendrite tip or to the mechanism of sidebranch appearance (see Refs. [13,14,16,17])). The development of simple phenomenological models based on a *minimum* number of statements, preferably the *most fundamental* ones,[5] can be a possible way out from the currently observed stagnation in the dendrite growth theory. The model shall be constructed *in general* for nonequilibrium solidification (because the dendrite is only one of many nonequilibrium shapes of growth; and according to the experiment, these shapes can be simultaneously observed in the course of nonequilibrium growth [18,19]). The development of such a phenomenological model is the objective hereof.

2. Model

The maximum entropy production principle, which is currently considered as one of the most important principles of nonequilibrium physics (see reviews [20–22]) finding increased usage in the problems of nonequilibrium crystallization [22–27], is chosen as a foundation. This principle can be most generally formulated as follows: at each level of description, with preset external constraints, the relationship between the cause and the response of a nonequilibrium system is established such as to maximize the entropy production. The maximum entropy production principle allows determining the dependency of thermodynamic fluxes on forces through maximization of the local entropy production[6] under the given thermodynamic forces. As a result, the principle leads to the equations describing heat/mass transfer (both molecular and convectional) which are traditionally used for the mathematical treatment of dendrite crystallization.

For the simplest one-component system solidifying from the supercooling melt, it is known (see e.g., Ref. [25]) that the local entropy production is proportional to the squared local rate of crystal growth V. Obviously, the supercooling Δ is the thermodynamic force here. For this simplest case, the maximization of the local entropy production agrees with the maximization V under the *given* (*fixed*) supercooling Δ:

$$V \to \max . \tag{1}$$

Thus, the condition (1) constitutes the foundation of the present model of nonequilibrium growth of a crystal (the dendrite, in the particular case). In anticipation of multiple criticisms regarding the statement (1), let us make a number of important notes explaining our viewpoint.

(1) The maximization of growing dendrite rate (1) was repeatedly used in the past, especially in the middle of the twentieth century [8,8,12,16,22,23,25]. Such an approach provides a quadratic dependency of rate on supercooling. However, this method was subsequently abandoned because the obtained results appeared to be in poor agreement with experiment: the growth rate was too high and the tip radius was too small. It is conventional to attribute the poor agreement with experiment specifically to the rate maximization procedure (1). However, it seems that the true reason may lie in the fact that the used models to which the maximization was applied misrepresented the real phenomena under consideration. Specifically, in the case of dendrite growth from the melt under terrestrial conditions, the convective heat transfer was obviously underestimated, which influence, according to the modern thorough experiments, is significant [13].

(2) As is known, MST is presently a common approach to describe the dendrite tip. This theory originated approximately thirty years after the disappointment in, and rejection of, the rate maximization principle. It is paradoxical that, in the course of the evolution of the theory, the founders of MST came to the conclusion that the solution describing dendrite growth at the maximum possible rate is the only linearly stable solution out of the discrete spectra of stationary "needle-shaped" solutions [11]. Thus, it turned out to be that the statement of rate maximality follows from MST! Here, it is appropriate to also note that some researchers (for example, E. Ben-Jacob [2]) seeing a number of problems in MST itself (specifically, in explaining the results of the anisotropic Hele-Shaw experiment) made the following statement: if more than one morphology is a possible solution, only the fastest growing morphology is nonlinearly stable and will be observed. So, as a result of the long-term intensive development of the dendrite growth theory, the researchers came back to the maximum growth rate principle.

(3) Whereas more than half a century ago the maximum rate principle appeared by intuition based on common sense, today it directly follows from the first principles of nonequilibrium thermodynamics (the maximum entropy production principle). That is an advantage of such an approach as compared to a number of modern theories of dendrite growth lacking any sound foundation.

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[2] There are only numerical and/or asymptotic dependencies.

[3] Here, the field of study based on and developed in the paper by Ivantsov [15] is meant. These studies represent the overwhelming majority and serve as a basis for multiple modern reviews, monographs, and textbooks on dendrite growth [11–13].

[4] Initially, a very particular model was chosen: an isothermal paraboloid growing at the constant rate in the medium due to heat conduction only. However, even this model itself had no analytical solution. Then, it has been "improved" and generalized for decades, which resulted in the avalanche-like growth of its mathematical complexity.

[5] Subsequently, if required, the model can be supplemented with assumptions taking into account the specifics of this or that nonequilibrium growth.

[6] In the general case, this dependency may be nonlinear.