Application of the Principle of Maximum Entropy Production to the Analysis of the Morphological Stability of a Growing Crystal

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Received December 20, 1999

1. INTRODUCTION

Questions concerning structure formation during continuous growth of a crystal are attracting a great deal of attention in connection with their theoretical and practical importance. Even though great progress has been made in this field after the publication of the classic works [1] and [2], many problems remain unresolved. We note here only two facts directly concerning the subject of the present paper.

1. A complete understanding of the relation between the conventional stability analysis (see, for example, [2, 3]) and the general principles of nonequilibrium thermodynamics is absent in the literature on crystallization. In most cases these approaches are either contrasted to one another or they are developed independently. Indeed, according to the theoretical works [4, 5] a fundamental principle in the development of a nonequilibrium system is the principle of maximum production of entropy. This principle can be formulated as follows: an arbitrary nonequilibrium system evolves toward a locally equilibrium state at an extremal rate (with maximum entropy production). Since this principle is important for the exposition, we shall discuss it in somewhat greater detail. The principle of the maximum rate of entropy production is proposed in [4] as a basis for the deductive construction of the thermodynamics of nonequilibrium processes. In this differential principle the fluxes which for fixed thermodynamic forces maximize entropy production are sought under quite general assumptions concerning the relations between the thermodynamic fluxes and forces. It is shown that this principle makes it possible to obtain all of the basic equations and laws of nonequilibrium thermodynamics and, specifically, other well-known variational formulations—the principles of Onsager, Biot, and Prigogine [4]. In [5] the apparatus of the phenomenological thermodynamics of irreversible processes is analyzed critically and another variational principle generalizing the preceding principles is advanced on the basis of the principle of local equilibrium. One consequence of the approach proposed in [5] is the confirmation of the extremal character of the rate of a transition of a dynamical system to a locally equilibrium state.

The principle studied in the present paper reduces, as will be shown below, in a particular case to the principle of the maximum possible local rate of growth of a crystal. However, the attitude of scientists concerned with crystallization toward the principle of maximum rate is extremely contradictory and changes with time. This is due primarily to the fact that the works [4, 5] have remained unnoticed, and this principle arose purely intuitively in the theory of crystal growth. The history of the application of the maximum-rate principle, specifically, with respect to the growth of a dendrite, is briefly as follows. Temkin seems to have been one of the first to use this principle in analytical calculations [6]. This principle was a criterion for selecting a definite solution from an entire family of possible solutions obtained in a phenomenological model. However, the experimental work [7] showed a substantial difference from the result obtained in [6] and the theoretical works [8, 9], based on a linear analysis of the stability of a growing paraboloid assuming isotropic surface tension, conversely, led to good agreement with exper-
As a result the latest theory [8, 9], which has been termed the theory of marginal stability, is contrasted with the principle of maximum rate of growth and, in consequence, the attitude developed that this principle is incorrect. However, in the opinion of the authors the discrepancy between the theory based on a maximality principle for selecting a definite solution and experiment could indicate, first and foremost, the coarseness of the model used in [6] as a basis for this theory. Approximately eight years later there appeared theoretical works indicating contradictions in the theory of marginal stability itself, specifically, the absence of a stationary solution corresponding to a needle-shaped dendrite. This led to the development of an improved theory in which weak anisotropy of surface tension was introduced (see the reviews [10, 11]). The new approach, known as the theory of microscopic solvability, also employs stability analysis. One result of this analysis was the assertion that a solution with the maximum rate of growth is the only stable solution from a discrete spectrum of stationary needle-like solutions. As the theory of microscopic solvability continued to advance, the problems of dendritic growth appeared to be largely solved. However, an experiment performed in an anisotropic Hele-Shaw cell and theoretical calculations in a boundary-layer model revealed a new problem: dendrites are not always observed in the case of weak anisotropy with decreasing supercooling/supersaturation [12–14]. As a result the tip of a dendrite splits. In [12–14], in order to get out of this contradiction, it is proposed that the criterion of solvability must be replaced by a more general criterion: the dynamically selected morphology is the most rapidly growing morphology. In other words, if the existence of more than one morphology is possible, only the most rapidly growing morphology is nonlinearly stable and therefore observable.

In summary, during the 30 years of study of the nonequilibrium crystal growth two approaches to the problem of morphology selection competed with one another: stability analysis and application of a maximality principle. Both principles are intuitively quite plausible. Even though the stability analysis in many cases leads to conclusions that the rate of growth is maximum, it seems obvious that in most cases each approach will lead, if not to qualitative then to quantitative differences. In our opinion, the search for the more “correct” approach is not promising; they should not be contrasted to one another, but rather an attempt should be made to find a logical relationship between them.

2. A large number of experimental and computer simulation works show that there exist ranges of the parameters where different morphologies can coexist [12–26]. Thus, in [22] two different types of disturbances started to develop simultaneously during crystallization of a melt of succinonitrile with additions of acetone, in the presence of definite supercooling, on a crystalline nucleus and coexistence of two forms of growth was observed: dendrites growing in the (100) and (111) directions. It is also remarked in the literature that the transition from one morphology to another accompanying a change in the parameters (for example, the supersaturation) can occur both with a jump in the rate or with a jump in its derivative [13–18]. On this basis an analogy is often drawn between phase and morphological diagrams and the concepts of first- and second-order morphological transitions are introduced [13–17, 27]. The most fundamental question arising in this formulation of the problem is finding the principle for selecting a possible morphology which would enable a complete calculate of a morphological diagram (with boundaries of metastable and labile regions). However, this problem has not been solved. In the literature it is hypothesized that far from equilibrium entropy production determines morphological selection but no specific calculations have been performed [13–15].

Thus, the goal of the present work can be formulated on the basis of the foregoing analysis (paragraphs 1 and 2): to study, using the principle of maximum entropy production, the problem of morphological selection during nonequilibrium growth of a crystal and to show, using the concept of morphological diagrams, the relationship between this approach and the stability analysis. For clarity this analysis is performed for the simplest problems: growth of a sphere, an infinite cylinder, and an infinite plane from a solution in the classic Mullins–Sekerka (MS) approximation [2].

2. PRINCIPLE OF MAXIMUM ENTROPY PRODUCTION IN CRYSTALLIZATION PROBLEMS

We shall study isothermal–isobaric crystallization as the most typical case and we shall assume that the growing crystal completely displaces the solvent. It is well known [28] that local entropy production $\sigma$ for the system under study equals

$$\sigma = I V \nabla \mu,$$

where $\nabla \mu$ and $I$ are, respectively, the gradient of the chemical potential and the flux of the crystallizing component. The expression (1) can be used for any elements of the volume under study and, specifically, for the region near the surface of a growing crystal. In this case

$$I = D(\nabla C)_{\text{int}} = (C - C_{\text{int}}) V,$$

where $C$ is the density of the crystal, $C_{\text{int}}$ is the concentration of the dissolved substance near a surface of arbitrary type, $V$ is the local growth rate, and $D$ is the diffusion coefficient.

We note that the entropy production (1) and (2) is proportional to the rate of increase of the mass of the growing crystal or, specifically, the velocity of the boundary. At the same time it contains an additional factor equal to the gradient of the chemical potential. Based on the investigations performed in [4, 5], the fol-