

From dendrites and *S*-shaped growth curves to the maximum entropy production principle

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S-shaped kinetic curves are very frequent in Nature. Based on our own experimental evidence on the growth of single dendrites and the literature data analysis, we have demonstrated that such curves may result from the maximum entropy production principle. The proposed approach also explains other prevalent laws of relaxation in nonequilibrium systems (Exponential, Kohlrausch, etc.).

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The dendrite growth is a typical example of self-organization. It occurs both in animate (e.g., trees) and inanimate nature (e.g., snowflakes) [1–3]. The shape similarity of such different objects may suggest some common laws of their evolution. Indeed, dendrites are formed in a nonequilibrium environment with relatively large gradients of concentrations, temperature, sunlight, etc. Therefore, some protuberances (formed, e.g., by chance) may grow faster in this inhomogeneous medium and a treelike structure appears [1–3]. One more startling similarity is true of the nonequilibrium evolution. That is resemblance of sigmoidal kinetic growth curves (*S*-shaped growth curves). However, this issue has received little attention. This question and its consequences are considered in the present paper.

Crystallization of ammonium chloride (NH_4Cl) from an aqueous solution was studied. The experimental conditions were considerably nonequilibrium: a solution saturated at 30–40 °C cooled down quickly to 10–20 °C to form dendrites (Fig.1). They were grown in quasi-two-dimensional conditions (a flat capillary whose thickness was much smaller than the diffusion length $\sim 400 \mu\text{m}$ was used) [4]. Consequently, the mass of the growing dendrite changed in proportion to its surface area in the plane of the experimental cell. A microscope with a photometry sensor built into the eyeglass was used. The integral light flux penetrating through the sample and hitting the photodetector was proportional to the surface area ratio of the solution and the crystal. The sensor signal was registered in the digital format (sampling frequency was 1 kHz). The mass was measured on a freely growing dendrite spaced at least the diffusion length from neighboring dendrites. Other experimental details have been published elsewhere [5, 6].

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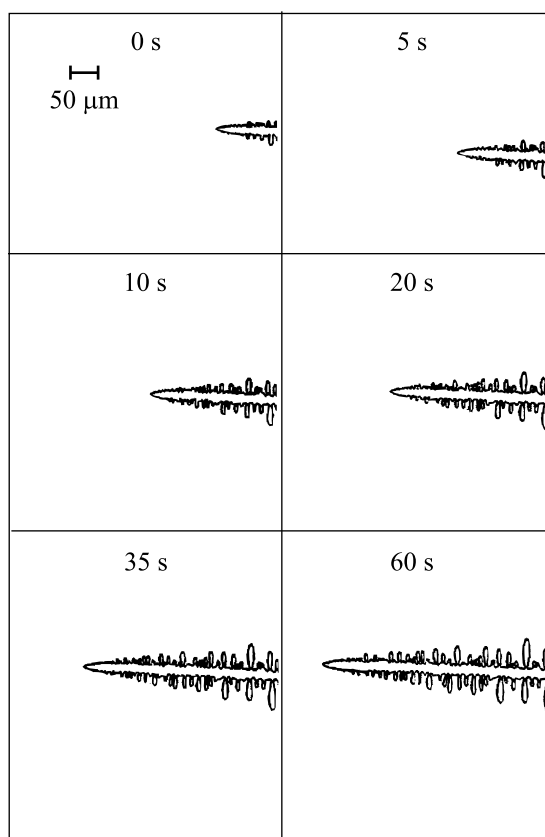


Fig.1. Growth of an NH_4Cl dendrite from an aqueous solution with time

The time-mass dependence had a specific *S*-shape at all the supersaturations and saturation temperatures (Fig.2). The growth time changed from several tens of seconds to several minutes only. Measurements were performed on over fifty growing crystals. The normalized data was subject to a regression analysis by the Levenberg-Marquardt method [7, 8] using the CurveEx-

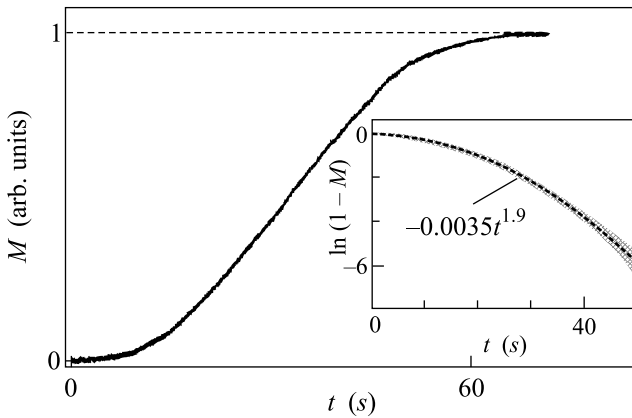


Fig.2. Typical experimental S-shaped kinetic curve: dendrite mass (M) vs. time (t). In the inset, gray curve represents $\ln(1 - M)$ vs. time; the broken curve is their fit using the power function

pert statistical software. A feature of the software was a large number of nonlinear regression models, which are most commonly used in applications. The aim of the analysis was to determine equations fitting the data best (the standard error of the estimate (E) and correlation coefficient (R) served as the “goodness of fit” [7, 8]). According to the calculations, the degree of supersaturation and saturation temperatures did not influence (within the experimental error) the regression models and their parameters. Therefore, all the data were integrated into one sample whose analysis yielded the following results.

The best fit (from the aforementioned criterion) provided the Weibull model $M(t) = a - b \exp(-ct^d)$ scoring 86 points (inset of the Fig.2 is additional argument for this model), the Richards model $M(t) = a/(1 + \exp(b - ct))^{1/d}$ scoring 122 points, and the MMF model $M(t) = (ab + ct^d)/(b + t^d)$ scoring 133 points. Some additional comments are necessary: (1) models having not more than four parameters (a , b , c , and d) were selected; (2) the points were equal to the sum of places (the place is higher if E is less and R is more) taken by a model fitting each experimental curve. This classification is very arbitrary and may provoke objections. Indeed, the correlation coefficients of the given models generally differ little (e.g., 0.993 and 0.994). With such “difference”, the physical interpretation of each model is most important. In this case, the Weibull model is well grounded theoretically as will be shown below.

The calculated Weibull model parameters were $a = 1.01 \pm 0.02$, $b = 1.00 \pm 0.02$, $c = 0.003 \pm 0.001$, and $d = 2.0 \pm 0.1$. Then the normalized experimental kinetic curves (see Fig.2) fit the model $M(t) = 1 - \exp(-ct^2)$ (the relative error of c is over 30% and this value is not substituted to the formula). Thanks to a greater body

of data and a larger sampling frequency of the signal digitizing, these data considerably refine those obtained earlier [5, 6].

The computed regression model agrees to within the denotation with the equation in the Kolmogorov–Avrami theory (KAT) for the time variation of the solid phase volume during mass crystallization [9–11]. This fact allows hypothesizing the applicability of this phenomenological stochastic-geometrical theory (used only in studies of mass crystallization of metals, polymers, etc. [9–11]) to description of the growth of single dendrites. Indeed, the particular case of this theory is the uniform nucleation of new phase nuclei in time and space, when the growth of each nucleus is diffusion limited (its linear size increase proportionally to the square root of time) [10]. Such nuclei may be secondary branches formed during the dendrite growth. These branches appear regularly on a growing primary branch and their growth is diffusion limited [1, 4]. They (“nuclei”) are nearly ellipsoidal in shape. According to KAT, at this two-dimensional growth d must be equal to two [10], which agrees fairly well with the experimental d value. In terms of KAT, it is possible to explain the dispersion of c values observed in experiment. This parameter (unlike d , which is controlled by the growth morphology) depends primarily on the occurrence rate of new nuclei and is very sensitive both to the growth time and initial conditions. Therefore, the correct determination of c calls for additional experiments with another experimental setup.

The modified KAT substantiates the choice of the Weibull model for fitting. This model should be preferred for one more important reason. Let us make two comments first.

1. The growth rate passes a maximum and approaches zero asymptotically during mass crystallization because crystals gradually fill all the vacant volume (adjacent nuclei collide and stop growing in the collision direction). This interpretation is incorrect for dendrite growth, which is decelerated due to the disappearance of solution supersaturation around a dendrite (the solution areas around dendrite branches “collide”).

2. $M(t)$ is the fraction of the solid phase during mass crystallization. Since nucleation sites are random, $M(t)$ may be taken as the probability that a random site crystallizes by the time t . In case of the dendrite growth the whole area is divided into two parts: (1) a crystal and a saturated (equilibrium) solution, and (2) a supersaturated solution. These parts have not a well-defined boundary. However, one may unambiguously distinguish the areas and watch their transition with time by setting a priori a concentration threshold slightly above the equilibrium. From the above reasoning $M(t)$ may

also be related to some area where supersaturation is removed and the chemical potential is nearly the same. Therefore, fraction $M(t)$ may be viewed (similarly to mass crystallization) as the probability of a transition at a random space site by the time t (the probability that the chemical potential of the site is equal to chemical potential of the dendrite crystal).

With this in mind, discuss Fig.2 again. Consider a random solution site. Let the time T of the transition at this site be a random variable. Then the probability that the transition occurs in a time T less than t equals $M(t)$ (which may be considered as a cumulative distribution function). Therefore, T obeys the Weibull distribution (since $d = 2$, it is also called the Rayleigh distribution) [12]. On the other hand the mathematical statistics [13, 14] suggests that minimums of random and bounded below variable have this distribution, i.e. if $T = \min\{T_1, T_2, \dots, T_n\}$ and $n \rightarrow \infty$ (T_1, \dots, T_n being identically distributed random variables equal to zero or larger), T will obey the Weibull distribution function. Therefore, one may hypothesize that the transition occurs in a minimum possible time or, in other words, mass or dendrite crystallization is realized at a maximum possible rate.

As is known, the crystallization rate is directly proportional to the entropy production in a system [15, 16]. This brings us to a notion known as the maximum entropy production principle (MEPP) [17–24]. It is used sometimes as the basis of the entire nonequilibrium thermodynamics (specifically, Prigogine's principle [15] was shown to be its corollary) [17, 18]. MEPP is widely used in natural sciences [17–20, 23], including crystallization [21–24]. However, earlier this principle was used theoretically and verified experimentally only in selection of solutions at bifurcation points (e.g., structures with a maximum rate (entropy production) were observed during nonequilibrium crystallization after morphological transitions) [19–24]. The foregoing suggests that the principle also holds for growth without sharp nonequilibrium transitions. A limitation of the proposed approach, as compared to KAT, is the impossibility to predict distribution parameters numerically. However, this problem is typical of every general theory (e.g., thermodynamics).

Our approach, which relates S -shaped growth curves, distribution of extreme values and MEPP, provides a unified viewpoint on numerous data about nonequilibrium kinetics and relaxation. Let us dwell on two points only.

1. S -shaped kinetic growth curves are observed in chemistry (the mass of reaction products vs. time) [25] and biology (number of bacteria and organism weight

vs. time) [26, 27]. Although such curves have particular explanations, they may result from MEPP too, especially if arguments are controversial. For example, S -shaped empirical kinetic curves in biology are frequently described by the Logistic model (Richards model with $a = d = 1$) [27]. However, this approach does not have solid theoretical grounds and has come under a storm of criticism [27]. Certainly, kinetic curves may be other than S -shaped (e.g., oscillation chemical reactions [15]). This fact does not disprove our approach or MEPP. Several simultaneous processes (each following MEPP) mutually interact and, therefore, kinetic curves change their shape [18].

2. Various relaxation phenomena in physics are considered using the exponential ($\sim \exp(-ct)$) and Kohlrausch ($\sim \exp(-ct^d)$) laws [28, 29]. These laws of the time perturbation dissipation are related to various physical mechanisms and are described by different models. However, they may also be viewed as the manifestation of a general law, namely MEPP. Indeed, relaxation may be considered either as disappearance of some parameter or its replacement by another parameter. In the latter case, normalized relaxation laws are $(1 - \exp(-ct))$ and $(1 - \exp(-ct^d))$ respectively. Consequently, the perturbation evolution laws follow the Weibull distribution and, therefore, may be considered as the MEPP corollary in the context of our approach.

In conclusion we shall emphasize that the proposed approach should not be considered as an antithesis to existing theories. Our approach provides a unified MEPP interpretation of many nonequilibrium natural phenomena (in turn, they can be viewed as indirect confirmation of MEPP).

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