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Transient from crystallization to fractal growth observed in both boar bile and SnI_2 vapour

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Abstract

A visual transient of the growth mechanism from crystallization to fractal growth was observed clearly in a drop of boar bile. The growing crystals were replaced by treelike fractal structures during solidification of the sample. It is fascinating to compare the transient with the result observed in SnI_2 vapour. They were completely identical, and revealed that under certain conditions a linear growth could be transferred spontaneously into nonlinear growth. It may be possible to consider the transient as a 'bridge' between linear and nonlinear growth, and to develop a quantitative expression of transient dynamics.

1. Introduction

Phase transition is one of the most fundamental and important topics in sciences, and linear equilibrium growth is an essential concept adopted widely [1–3]. Fractal growth far from equilibrium is another kind of important concept developed recently, which is related to nonlinear theory. The fractal is no longer a novel concept since it was suggested by Mandelbrot in 1982 [4]. Fractals usually display randomly ramified patterns (self-similarity) and no characteristic length (scale-invariance), and can be found in nature or in experimental systems. Fractal patterns can also be observed by computer simulation results [5, 6]. The formation of random branching structures in thin solid films was observed previously in different systems and over many length scales, such as electrochemical deposition [7–9] and growth during vapour–solid transformation [10].

The majority of the latest experiments, however, have been designed to produce data for additional theoretical research and to check the validity of various predictions. The most suitable systems to carry out this kind of investigation are those in which the behaviour of

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the growing interface is determined by a relatively small number of well defined parameters. The most studied further phenomena leading to complex interfacial patterns are crystallization (instead of solidification) and electrodeposition. In the above mentioned experiments the motion of the interface is dominated by a quantity which in various approximations satisfies the Laplace equation; therefore, they are known as experiments on Laplacian growth [11].

A large number of scientists are focusing their interests on the relationship between linear growth (crystallization) and nonlinear growth (fractal). A question may arise: could both linear growth and nonlinear growth occur in a system? The following test shows unexpected amusing results that were observed in both a biological system and a physical system.

2. Experimental details

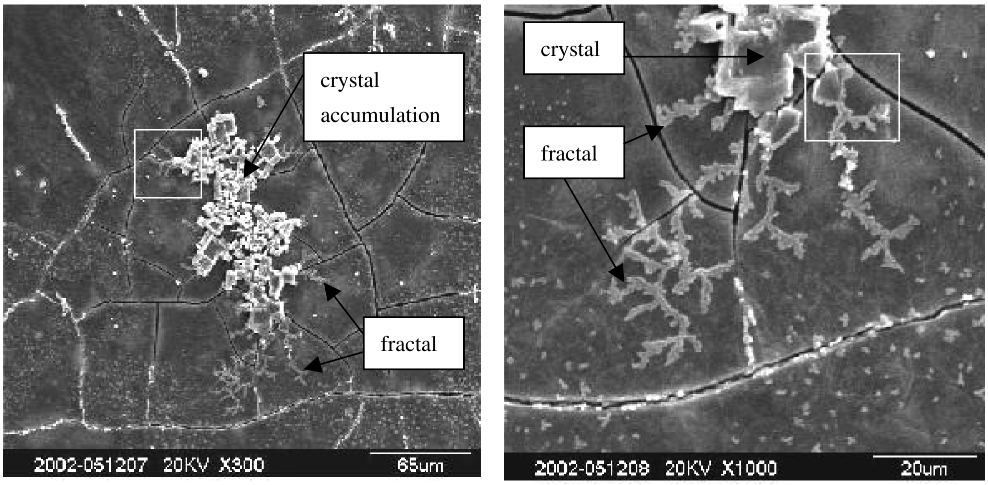
A piece of glass plate was used as the carrier of a drop of boar bile. Before dropping the boar bile on the surface of the glass plate, a hydrophilic treatment was performed on the glass plate. 25 μl fresh liquid bile of a one-year-old healthy boar was dropped on the surface of the treated glass plate, and kept in a dry chamber at 18 °C for three days. The relative humidity in the dry chamber was kept at 40%. The air above the sample in the dry chamber was forced to flow slowly at a speed of around 5 cm s^{-1}. The dried bile sample was taken out from the dry chamber, and coated with 10 nm thick gold film for conducting in a vacuum film deposition equipment. The sample was analysed by both the field emission gun–scanning electron microscope (FEG–SEM), model JSM-6301F, JEOL, and scanning electron microscope (SEM), model S-450, Hitachi. The chemical compositions of the precipitate and boar bile matrix were measured by energy dispersive x-ray spectroscopy (EDS) attached to the FEG–SEM. All elements were analysed and normalized.

3. Results and discussion

3.1. Transient observed in the boar bile

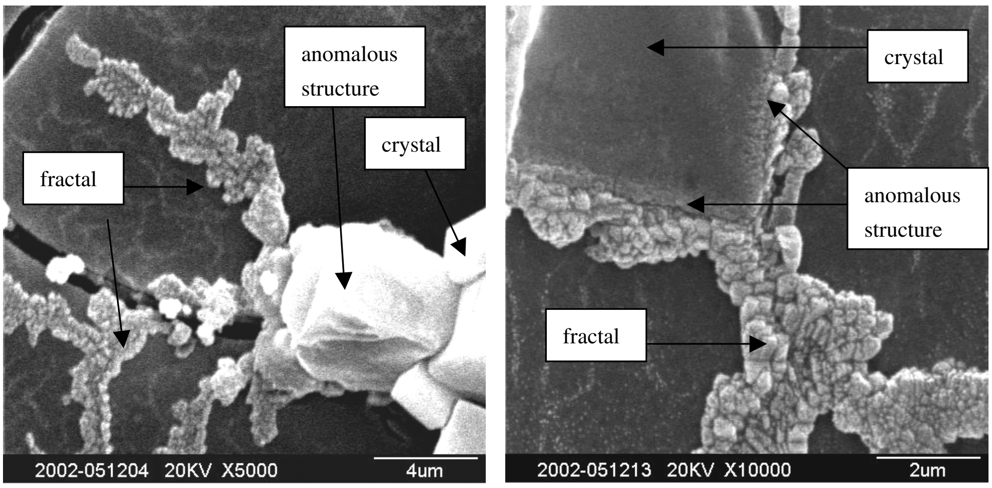
A large number of precipitates on the surface of the bile sample were observed by FEG–SEM. Figure 1(a) shows the FEG–SEM image of a precipitate under a magnification of 300 times. It contained two parts, i.e., the crystals of precipitate and surrounding ramified structures. The crystals of the precipitate aggregated together and formed a crystal accumulation that located at the centre of image. The ramified structures grew up at the advancing front of the crystal accumulation. They displayed self-similarity and scale-invariance to a certain extent, and were a typical kind of fractal structure. Several microcracks surrounding the whole image of the precipitate were observed, which formed during coating a layer of gold film on the sample. The longitudinal size of the crystal accumulation of the precipitate was about 157 μm, and that of the longest fractal structure was around 50 μm.

It is clear from figure 1(a) that the transient from crystallization to fractal growth took place spontaneously in the liquid boar bile during preparation of the sample. In other words, there was a transient from linear equilibrium growth (crystalline growth) to nonlinear non-equilibrium growth (fractal growth). As a result of the transient, the randomly ramified structures must grow up at the advancing front of the crystal accumulation, as shown in figure 1(b). It is reasonable to deduce that the fractal growth followed the crystalline growth, and can be called the second stage of the dynamical growth process. It is also deduced that a transfer region between crystallization and fractal growth should exist even though it might be very narrow. Figure 2(a) is the closer view of the pattern shown in the upper-left corner of figure 1(a). It shows three kinds of structure of the precipitates, i.e., the crystals, the anomalous structure



(a) (b)

Figure 1. (a) FEG–SEM image of crystal accumulation and fractal structures of precipitates in the boar bile; (b) closer view of the branches at the bottom of the image shown in (a).



(a) (b)

Figure 2. Closer views of the transfer regions (a) shown at the upper-left corner of figure 1(a) and (b) shown at the upper-right corner of figure 1(b).

and the fractal structure. The crystals were of regular shapes, and four of them are displayed near the right margin of the image. The anomalous structure that linked the crystals and fractal structures was of irregular shape and strange morphology. The fractal structure consisted of numerous small grains, and its surface was very uneven. It can be found in figure 2(a) that there is a continuous decrease of crystal size as diffusion becomes slower. Figure 2(b) is the closer view of the pattern shown in the upper-right corner of figure 1(b). It also shows three kinds of

Table 1. Compositions of the crystal, fractal structure and boar bile matrix by EDS analysis (at.%).

Element	Crystal	Fractal structure	Boar bile matrix
C	64.38	62.54	68.09
O	32.39	33.84	25.96
Na	2.22	2.45	3.80
Cl	0.70	0.62	1.32
K	0.14	0.22	0.32
Ca	0.00	0.08	0.08
Au	0.17	0.25	0.43
Totals	100.00	100.00	100.00

structure: the regular crystal, the anomalous structure and the fractal structure. The anomalous structure magnified 10 000 times also linked the crystals and fractal structures. It located along the edges of the boundary crystal, and obviously demonstrates a transfer region. Comparing figures 2(a) and (b), it can be seen that the morphologies of both anomalous structures were different. However, they implied that a transfer region did exist for the transient.

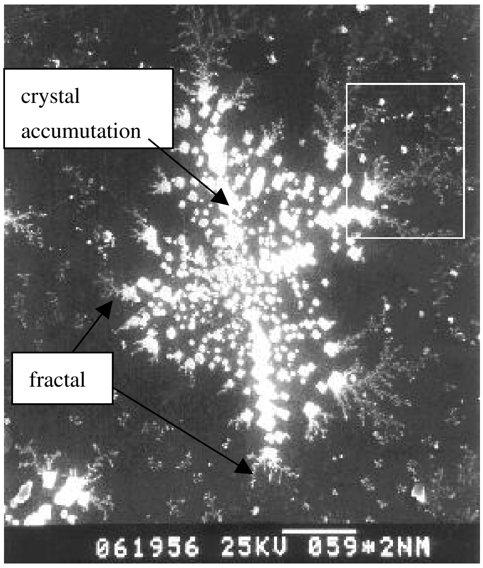
EDS analysis was performed on the crystal, a branch of the fractal structure and the bile matrix shown in figure 1(a), respectively. The chemical compositions of the three EDS spectra are listed in table 1. It can be seen from table 1 that there is not much difference between the composition of the crystal and that of the fractal structure. But, there is a bigger difference in contents of C, O, Na, Cl and K elements between the precipitates (crystal and fractal structure) and bile matrix. The gold in table 1 came from the deposited Au film. In general, boar bile is composed of glycoprotein, cholesterol, lecithin, bilirubin etc. The EDS data show that both the crystal and fractal structure consisted mainly of complex molecules of organic compounds.

It is possible to explain the transient in terms of solute molecules or ions in the bile system. At the first stage of the precipitation process, there were plenty of various solute molecules or ions around each nucleation site, and the crystals grew up quickly. Later, the concentration of solute molecules or ions surrounding each crystal decreased slowly because of crystallization. The liquid bile sample was gradually thickening due to evaporation, which in turn resulted in weak diffusion of solute molecules or ions. Finally both factors, crystallization and the weak diffusion rate, resulted in a shortage of solute molecules or ions that were necessary to the crystallization. At the second stage, the crystalline growth was arrested, and the fractal growth started, i.e., a transient from crystallization to fractal growth took place.

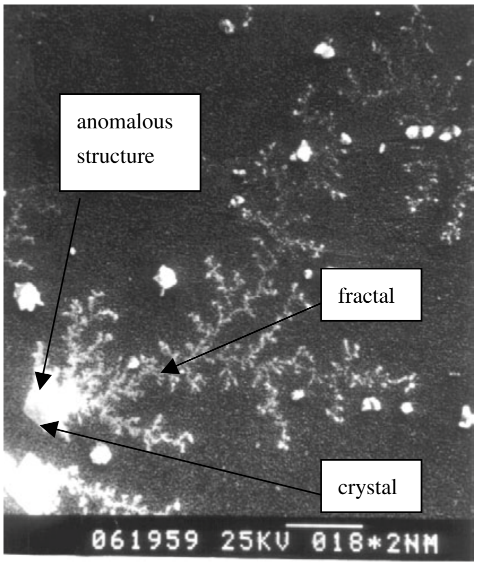
3.2. Transient observed in SnI_2 vapour

It is interesting to compare the experimental result obtained in the bile sample with one found in SnI_2 vapour that was investigated previously [12]. A completely identical transient of the growth mechanism was observed in SnI_2 vapour. The experimental set-up used in this work was an evaporation–deposition device. High-purity SnI_2 powder was chosen as the source material of the evaporator. A silicon wafer was selected as the carrier of the SnI_2 deposit and cleaned by a dilute HF (1:10) dip. The Si wafer was loaded into the deposition chamber that was heated at 520 °C for 1 h. SnI_2 molecules evaporated from the evaporator moved randomly in the whole space of the deposition chamber, and some of them deposited on the surface of the Si wafer. The sample was subsequently cooled with a rate of 1000 °C min^{-1}.

Some fascinating and valued SEM images were obtained. Figure 3 shows two SEM images of the SnI_2 deposit. It can be seen clearly in figure 3(a) that there is a SnI_2 crystal accumulation in the central zone. Many spreading ramified branches can be observed at the



(a)



(b)

Figure 3. (a) SEM image of SnI_2 crystal accumulation and fractal structures; (b) closer view of a branch at the upper-right corner of the image shown in (a).

advancing front of SnI_2 crystal accumulation. These randomly ramified branches grew and spread out from the edges of the boundary crystals. Figure 3(b) is the closer view of a branch shown in the upper-right corner of figure 3(a). The treelike ramified structures magnified 8000 times displayed self-similarity and scale-invariance, and were a kind of fractal structure. An anomalous structure linking smoothly the crystal and fractal structures is also observed clearly in figure 3(b). It confirms that there was a transfer region between the crystallization and fractal growth. Figure 3 shows a continuous decrease of crystal size as diffusion becomes slower.

A growth process similar to one occurring in the bile system took place in the SnI_2 evaporation–deposition system. At the first stage of the SnI_2 deposition process, the SnI_2 crystals grew up continuously because of enough SnI_2 molecules surrounding each SnI_2 crystal. When cooling the sample, the concentration of SnI_2 molecules decreased dramatically because of the higher cooling rate. There were not enough SnI_2 molecules available for SnI_2 crystalline growth. At the second stage, the crystalline growth of SnI_2 was transferred spontaneously to fractal growth.

Two identical experimental results were obtained from two completely independent distinct systems, i.e., a biological system and a physical system. It is also pointed out that the transient was independent of the sample's carrier, as shown in table 2. The experimental results imply that the transient is one of the inherent features in certain dynamical systems, and can be described as a 'bridge' between linear equilibrium growth and nonlinear non-equilibrium growth. It is worth noting that the changes of entropy production accompanying crystallization and fractal growth, respectively, were completely opposite. According qualitatively to the general principles, the entropy production was positive for crystalline growth, and negative for fractal growth. This can be explained briefly as follows.

Table 2. Comparison between the boar bile test and SnI_2 deposition test.

Items	Boar bile test	SnI_2 deposition test
Kind of system	Biological system	Physical system
Carrier of sample	Glass (amorphous)	Si wafer (single crystal)
Phase transition	Liquid state to solid state	Gaseous state to solid state
Temperature and duration	at 18 °C for three days	at 520 °C for 1 h
Crystal kind of precipitate	Complicated organic crystal	Simple inorganic crystal
Max. size of crystal accumulation (μm)	157	30
Max. size of fractal structure (μm)	50	12

Assume S is the entropy of a system, and $\mathrm{d}S$ the change of the entropy. Then, $\mathrm{d}S$ can be expressed as

$$\mathrm{d}S = d_i S + d_e S \tag{1}$$

where $d_i S$, entropy production, is produced due to an irreversible process occurring in the system, and $d_e S$, entropy flow, is produced due to interaction between the system and the outside environment.

When an irreversible process takes place in the system, such as a crystallization process, then

$$d_i S > 0. \tag{2}$$

For a non-equilibrium growth, the principle of minimum entropy production was suggested by Prigogine in 1945 [13, 14]. Assume T ($T > 0$) is the total entropy production in a system which is in non-equilibrium state. The following results have been obtained [13].

$$\text{For stationary state} \qquad \mathrm{d}T/\mathrm{d}t = 0 \tag{3}$$

$$\text{For off-stationary state} \qquad \mathrm{d}T/\mathrm{d}t < 0 \tag{4}$$

where t is time. From inequality (4), it is easy to work out inequality (5), as follows:

$$\mathrm{d}T < 0. \tag{5}$$

It is reasonable to assume that a transformation of entropy production from positive to negative should take place at the transfer region. The experimental results evidence the complex behaviour of simple systems, provide a major impetus in research and led to our improved understanding of transition and critical phenomenon. It is foreseen that similar results could be found in other systems, whether liquid or gaseous state, and organic or inorganic compounds, if the concentration of molecules or ions necessary to crystalline growth decreases dramatically.

4. Summary

In summary, we suggest an empirical model for the transient as follows. During a phase transition performed in a liquid or gaseous system, if the concentration of molecules or ions necessary to crystalline growth is dramatically in short supply due to certain factors, then a transient of the growth mechanism from linear equilibrium growth to nonlinear non-equilibrium growth will occur. A spreading fractal growth will replace spontaneously regular crystalline growth. There must be a transfer region between crystallization and fractal growth.

Acknowledgments

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