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Self-affine fractal crystal from an NH_4Cl solution

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A random interface of growing crystal is experimentally studied in a two dimensional system. The crystal grows from an NH_4Cl solution and is polycrystalline, composed of many grains. The interface is rough and self-affine fractal. The roughness exponent is in the range of 0.79–0.91, where the average value is nearly 0.83.

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INTRODUCTION

Nature creates many dynamical random patterns and some of them have been studied in terms of self-affine fractals during the past decade [1]. Mandelbrot has developed the notation theoretically and discussed some relations between the self-affine fractals and the self-similar fractals [2]. Kadar, Parisi, and Zhang have also developed an analytic model for growing interfaces (KPZ equation [3]) and many simulations have been done [1]. They reveal the roughness exponent α is 0.5 in two dimensional self-affine fractal objects in the presence of Gaussian noise, and this property is called a universality. However, some experimental results in a two dimensional system show α is larger than 0.5; Rubio *et al.* have obtained $\alpha=0.73\pm0.03$ in wetting immiscible viscous flows in porous media [4], Vicsek, Cserzö, and Horváth have obtained $\alpha\simeq0.78$ in bacterial colonies [5], and Horváth, Family, and Vicsek obtained $\alpha\cong0.81$ in viscous flows in porous media [6]. For the explanation of the experimental results Zhang has proposed the noise not of the Gaussian but of a power law distribution [7]. Csahók, Honda, and Vicsek have also obtained $\alpha=0.75$ from a KPZ type equation with quenched additive noise from a dimensional analysis of the equation [8].

On the other hand, crystal growth shows many various growing patterns, and Licoppe, Nissim, and d'Anterroches have obtained $\alpha\simeq0.5$ in two dimensional solid-state recrystallization of amorphous GaAs films observing with an electron microscope [9]. We report a different subsequent crystal growth of a self-affine fractal. Leaving a nonsupersaturated NH_4Cl solution whose solvent is water in a beaker for a long time, an NH_4Cl crystal grows up the inner wall of the beaker. The crystal grows as a thin film and the surface is random. We can also observe the three dimensional random growth from the bottom simultaneously. The NH_4Cl solution flows from the back of the interface and this is different from the usual crystal growth. This phenomenon results from the supersaturation by natural evaporation of the NH_4Cl solution. The crystal is polycrystalline, composed of many grains and the NH_4Cl solution rises up by capillarity through the grain boundaries. We have investigated the growing pattern experimentally and report the roughness exponent of the interface.

EXPERIMENT AND RESULTS

An NH_4Cl solution whose solvent is water is in a cubic cell (outer size is $17\times17\times17$ mm^3). The bottom of the cell is open and attached to a sapphire glass. Four square holes (50 μm$\times$7mm) are made in each bottom side of the cell. The saturated temperature of the NH_4Cl solution is 40 °C and the temperature of the sapphire glass is controlled at 40.42 ± 0.02 °C. First, the NH_4Cl solution soaks out of the holes just a little, and the solution evaporates and is supersaturated soon because of the hot sapphire glass. Second, the nucleations of NH_4Cl crystals occur in the supersaturated solution and the crystal grows horizontally. As the NH_4Cl solution flows from the cell to the crystal interface, the crystal continues to grow. We observe the growing behavior with a microscope and take the pictures with a videotape recorder, and they are processed by image analysis. The control parameters are the temperature and the concentration of the solution and we fix the values as the above ones in this experiment.

We show a typical growing pattern in Fig. 1, which is printed out from the videotape recorder. The crystal is polycrystalline and there exist many grain boundaries. The solution flows with capillarity through the grain boundaries from the cell, which are seen in black in Fig. 1.

We show successive growing patterns of the interface every 10 sec in Fig. 2, which is processed by image analysis. The growth direction is upwards and the scale unit is the dot of the image. The interface has 480 dots and the distance between two dots corresponds to 2.05

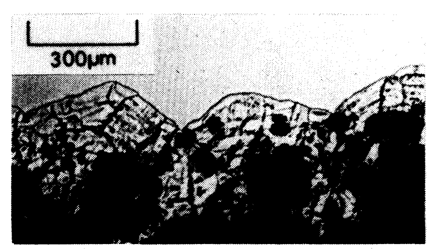

FIG. 1. Typical growing pattern printed out from videotape recorder. The crystal is polycrystalline, with many grains which make a complicated network. An NH_4Cl solution flows through it, which is seen in black.

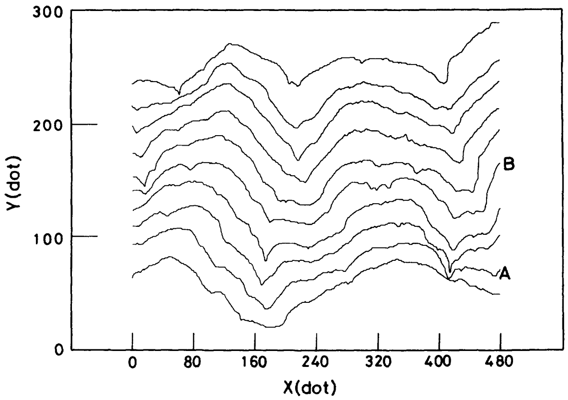

FIG. 2. Successive interfaces shown every 10 sec processed with image analysis. The growth direction is upwards. Horizontal full scale is 480 dots and corresponds to 0.982 mm.

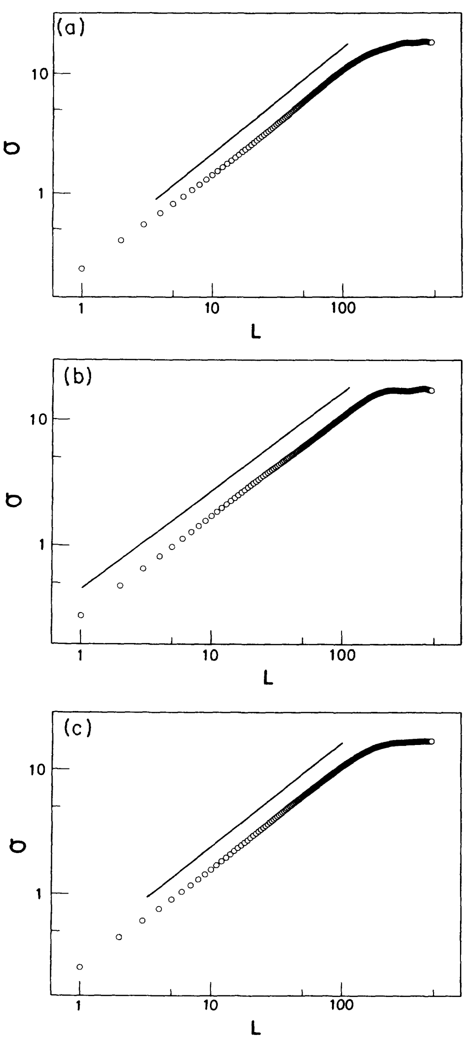

FIG. 3. (a) Standard deviation σ vs scale length L of interface A of Fig. 2. The unit is the dot of the image. The least-squares fit to the linear region results in $\alpha \simeq 0.89$, whose slope is given with a solid line. (b) Standard deviation σ vs scale length L of interface B of Fig. 2. $\alpha \simeq 0.79$. (c) Standard deviation σ vs scale length L averaging all the interfaces of Fig. 2. $\alpha \simeq 0.83$.

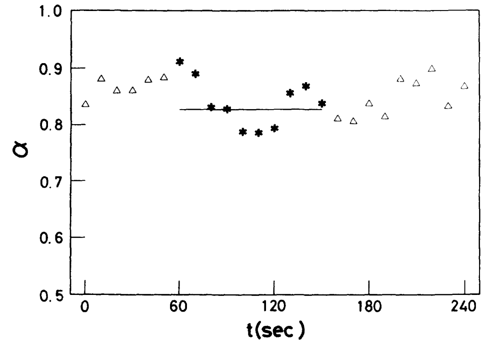

FIG. 4. Roughness exponents α vs growth time t shown every 10 sec. The values are limited within 0.79 and 0.91. * symbols correspond to interfaces in Fig. 2 and the solid line is for the average value 0.83.

μm. Then, the horizontal full scale is 0.982 mm. The average growing velocity of the interface is 4.47 μm/sec ($=2.18$ dots/sec).

In Figs. 3(a) and 3(b), we show the relations (log-log plots) between the average standard deviation $\sigma(L)$ and the length of the interval L about the interfaces A ($t=70$ sec) and B ($t=100$ sec) of Fig. 2, respectively. Their roughness exponents are nearly 0.89 and 0.79; the slopes are shown with solid lines to guide the eye. The scale unit is also the dot of the image. We show the same average relation of the all interfaces of Fig. 2 in Fig. 3(c), and the average roughness exponent is nearly 0.83.

We show the roughness exponents against the growth time (every 10 sec) in Fig. 4. The exponents of the interfaces of Fig. 2 are shown with the * symbol and their average value is given with a solid line. Their minimum and maximum values are 0.79 and 0.91, respectively.

DISCUSSION

The solution flows from the back of the growing interface and this is different from usual crystal growth. When the crystal grows, the solution wets the growing interface. Indeed, we can observe a very thin remaining film at the front of the interface after the crystal growth is finished. We believe that the fundamental growing mechanism is a lateral growth, even though the direct observation of running steps has not been achieved. We observe that the interface grows relative to the lateral direction against the average growth direction. The grain boundaries make a complicated network where the solution flows (Fig. 1). The local growth velocity of each grain depends on the flowing quantity of the solution through the network, which is different among the grains. This results in the rough surface. When there exists a large difference among the local velocities of the grains, we can observe overhangs of the interface; however, there is no overhang in this experiment. As the solution comes from the back of the interface, the grains at the rear of the interface also grow vertically just a little and become thicker. However, the thickness of the growing interface is of order μm and our system is two dimensional. The measured range is limited within 1 mm; however, the global pattern grows up to the order of centimeters.

The control parameters are the temperature and the concentration of the solution. On the other hand, the growth may also depend on the atmospheric pressure and the kind of plate where the crystal grows. The pressure is about 1 atm and we suppose that there is no necessity for its precise control in this experiment. However, the growth may intensely depend on the plate because the behavior of the wetting of the solution depends on the surface tension between the solution and the plate. This remains to be cleared up.

The average roughness exponent is obtained about the interfaces of Fig. 2; 60 sec $\leq t \leq 150$ sec. Because of the scaling, the linear regions and the standard deviations at the upper limit are relatively similar as shown in Figs. 3(a) and 3(b); $\sigma(100) \sim 10$ dots. However, in a case of $t = 210$ sec, e.g., $\sigma(100) \sim 7$ dots. The values of the roughness exponents are within 0.79 and 0.91 and the average roughness exponent is nearly 0.83, which is larger than 0.5 as reported in Refs. [4–6].

According to the model of Zhang [7], the larger roughness exponent is derived dependent on the scaling parameter of the noise with a power law. The larger exponent arises from the local rare thrust of the interface, which has the following effects: (1) the thrust expands laterally to cover its neighboring region (amplification effect) and (2) the thrust results in a hill on the interface and the geometry is remembered for a long time (memory effect). In our experiment, from that qualitative viewpoint, the interface has many small and large dents (Fig. 2). The dents correspond to the thrusts of Zhang's model because they also have the same amplification and memory effects if the growth direction in Fig. 2 is seen downwards in reverse. The scales of the larger grains are about 150 dots (~ 300 μm). When they collide with the others, there appear larger dents. Furthermore, the larger domain is composed of many smaller grains. And they also make smaller dents and influence the same effects on a smaller scale as larger dents.

On the other hand, as Csahók, Honda, and Vicsek have pointed out, there exist pinning forces in many self-affine experimental situations, which make thrusts or dents in the interfaces [8]. Furthermore, from the simulation of the KPZ type continuum equation with quenched additive noise, they have shown that there exist pinning forces in their model. Our dents could also be understood as resulting from the pinning forces phenomenologically. Eventually, we believe that the interfacial roughness and the self-affinity results from the factors mentioned in the above qualitative discussion: the dents corresponding to the thrusts or the pinning forces. However, we cannot judge at the present time which model is the best to explain our experimental results. In order to do this, we must measure a growth exponent β; e.g., Csahók, Honda, and Vicsek have obtained $\beta = 0.6$ in a two dimensional system [8]. Incidentally, comparing our result ($\alpha = 0.83$) with their result ($\alpha = 0.75$), our result is a little larger.

As obtained by Mandelbrot [2], the roughness exponent α is related to the fractal dimension such as the divider dimension D_d or box dimension D_b, e.g., $D_d = 1/\alpha$ and $D_b = 2 - \alpha$. We obtain the divider dimension $D_d \simeq 1.11$ about the interfaces of Fig. 2 and $1/D_d \simeq 0.90 \sim \alpha$. Because the dot number of the interface is not so large (480 dots), the error is large; however, the above relation may be confirmed.

CONCLUSION

Rough interfaces of growing NH_4Cl crystal are experimentally studied in a two dimensional system. The growth is concerned with wetting and evaporation, and the growing mechanism is lateral growth. The crystal is polycrystalline, composed of many grains. The interface is self-affine fractal and the roughness exponent is in the range of 0.79–0.91, where the average value is about 0.83.

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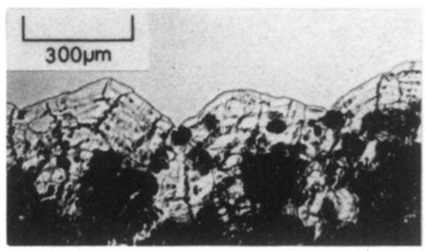

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