Monte Carlo Simulation of the Crystal Growth

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The poly-nuclear growth model (PNG) and the Monte Carlo (MC) simulations are described and discussed. Results prove that our MC simulation provides a good agreement with an analytical model proposed for the infinite system.

§1. Introduction

The layer by layer growth of metal from an electrochemical solution was demonstrated by Bostanov et al. [1]from the oscillatory nature of the initial growth kinetics. This oscillatory evaporation transient was measured clearly in a molecular beam system. [2] The lamellar morphology is well established in both single polymer crystals grown from solution and melt grown crystals. Goldenfeld derived an exact expression for the linear growth rate of two-dimensional nucleation controlled crystal growth.[3] The growth rate was also derived independently by Bennett et al.[4]

Recently, Gilmer has carried out the Monte Carlo (MC) simulation to calculate these transients and discussed the growth rate, comparing the results with those analytically obtained from the poly-nuclear growth (PNG) model.[5] The PNG model has attracted much attention in the field of crystal growth and ferroelectric domain wall motion.[1-11] Ishibashi and Orihara have proposed an analytical model, which has been found to provide a better agreement than those so far presented with the MC result of the growth transient.[10,11] They have been presented the characteristics of a PNG model not only for the two-dimensional case, but also the one dimensional one. However, Ishibashi-Orihara (IO) model for the one dimensional case was inconsistent about 7% with the exact solution.[4,12,13] The purpose of this paper is to present the MC simulation results for the one-and two-dimensional cases. In order to examine the IO model, which was given for the infinite system, our MC simulation was performed for the infinite limit of the crystal growth transients. We also made the calculation with several parameters to examine the analytical model given for the one dimensional case.

We will review the analytical models in §2 and §3. In §4, we introduce the MC simulation method given by Gilmer. Our result and discussion will be given in §5 and §6.

§2. Analytical Models of the PNG Transients (IO model)

Let us denote by c_n the fraction of grown area in the n-th layer, which gives a probability that a point P in the n-th layer is included in the grown crystal.[10,11] The probability for P not to be included in the grown crystal, $1-c_n$, is given as

$$1-c_n(t)=1-c_{n-1}(t)+c_{n-1}(t) \times \prod_{i=0}^{j}[1-JS(j\Delta\tau, i\Delta\tau)c_{n-1}(i\Delta\tau)\Delta\tau] \quad (1)$$

where the Kolmogorov method is adopted to determine the II term.[14] $S(j\Delta\tau, i\Delta\tau)$ is the area covered at t by a nucleus born at τ. The eq. (1) can be transformed to

$$c_n(t)=c_{n-1}(t)\{1-\exp[-\pi Jv^2\int_0^t(t-v)^2 \times c_{n-1}(\tau)d\tau]\}, \quad (2)$$

where

$$c_0(t)=1. \quad (3)$$

The growth rate

$$R(t)=\sum_{m=1}^{\infty}\frac{dc_m(t)}{dt} \quad (4)$$

numerically obtained is shown in Fig. 1, where the results based on the Borovinskii-Tsindergozen (BT) model[15]

$$c_n(t)=1-\exp\{-\pi Jv^2\int_0^t(t-\tau)^2c_{n-1}(\tau)dt\} \quad (5)$$

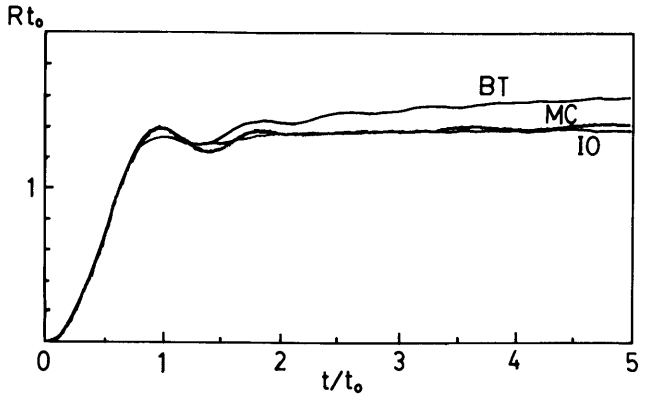

Fig. 1 The growth rate Rt_0 in the two-dimensional case. BT indicates the result by the Borovinskii-Tsindergozen model, and IO is the one given by Ishibashi and Orihara. MC is our result calculated by the Monte Carlo simulation.

is also presented. With respect to $R(t)$, IO model shows a better agreement than the BT model with the MC result presented by Gilmer, which is discussed in §4.

The $R(t)$ obtained from the one dimensional case is given as

$$c_n(t) = 1 - \exp[-2Jv\int_o^t (t-\tau)c_{n-1}(\tau)d\tau], \quad (6)$$

§3. Kinetic Theory on a One Dimensional Growth of a Finite length

Frank analyzed the kinetics of crystal growth.[13] Now, we review his model. The growth is assumed to be controlled by a constant nucleation events of the thickness b on the edge of the lamella ; the new layer then grows in both directions with a constant velocity v. When the growth step either reaches the end of its substrate, of length L, or meets an independently nucleated growth layer at the same level, this growth will stop. Nucleation occurs randomly anywhere within L at a mean rate of J nucleation events per unit length and time. It is evident that if $v/L \ll JL$, the growth of a layer will usually be completed before another is nucleated, and, in the limit, the growth rate will be

$$G = b\ J\ L, \quad (7)$$

independent of v. On the other hand, if this strong inequality is not satisfied, several nucleation events may share responsibility for one layer, so that the growth rate is less, which should approximate

$$G = b(jv)^{1/2}. \quad (8)$$

He solved the general cases as follows : Each nucleation event in the substrate domain $-(1/2)L < x < (1/2)L$ create a pair of steps, respectively facing and traveling to the left and to the right with velocity v. There are, in ensemble average, $l(x)$ of the former and $r(x)$ of the latter per unit length. A step of double height is counted as two steps. Since no steps enter from outside the limits $x = \pm (1/2)L$, we have

$$l\{x=(1/2)L\} = r\{x=-(1/2)L\} = 0\,, \quad (9)$$

and, between these limits ;

$$\partial l/\partial t = J + v(\partial l/\partial x) - 2vlr, \quad (10)$$

$$\partial r/\partial t = J - v(\partial r/\partial x) - 2vlr, \quad (11)$$

in which the term on the right represent initiation, drift, and annihilation of steps, respectively.

It is assumed that a steady state can be attained in the ensemble average in which case eq. (4) and eq. (5) are to be equated to zero. Then

$$\mathrm{d}l/\mathrm{d}x = -J/v + 2lr = -\mathrm{d}r/\mathrm{d}x. \quad (12)$$

Hence,

$$\mathrm{d}(l+r)/\mathrm{d}x = 0\,. \quad (13)$$

So that

$$l + r = 2c, \quad (14)$$

a constant.

By symmetry;

$$l(x=0) = r(x=0) = c. \quad (15)$$

Combining (12) and (14) ;

$$\mathrm{d}l/\mathrm{d}x = -J/v + 4cl - 2l^2. \quad (16)$$

The solution of this equation is obtained by quadrature, using (15) to determine an integration constant, as

$$-x = \{1/2(J/2v - c^2)^{(1/2)}\} \text{ arc tan } \{(1-c)/(J/2v - c^2)^{(1/2)}\} \quad (17)$$

He introduced for convenience sake,

$$Q = (P^2 - L^2c^2)^{1/2} \quad (18)$$

where

$$P = L(J/2v)^{1/2} = (2z)^{1/2} \quad (19)$$

being the parameter used by Lauritzen.[12] In these terms (7) rearranges to

$$l = c - (Q/L) \tan (2Qx/L). \quad (20)$$

The boundary condition (9) becomes

$$Lc = Q \tan Q. \quad (21)$$

Then the growth rate is solved as

$$G=2bcv. \tag{22}$$

As the easiest method of calculation from these equations in the general case, he assumed a value of Q, and deduced from it Lc, and

$$P=Q \sec Q. \tag{23}$$

For small Q we have the approximations

$$Lc=Q^2(1+(1/3)Q^2+(2/15)Q^4+\ldots), \tag{24}$$

$$P^2=Q^2(1+Q^2+(2/3)Q^4+\ldots), \tag{25}$$

so that

$$Lc=P^2(1-(2/3)P^2+\ldots), \tag{26}$$

giving

$$G=bLJ(1-L^2J/2v+\ldots), \tag{27}$$

in agreement with (7).

For Q approaching $\pi/2$ we have :

$$Q=\pi/2-\delta \tag{28}$$

$$Lc=(\pi/2-\delta)\cot\delta$$
$$=(\pi/2\delta-1)(1-(1/3)\delta^2-(1/45)\delta^4-\ldots). \tag{29}$$

$$P=(\pi/2-\delta)\operatorname{cosec}\delta$$
$$=(\pi/2\delta-1)(1+(1/6)\delta^2+(7/360)\delta^4+\ldots). \tag{30}$$

So that

$$Lc=P(1-\pi^2/8P^2-\ldots). \tag{31}$$

giving

$$G=b(2Jv)^{1/2}(1-\pi^2v/4L^2J-\ldots), \tag{32}$$

which agrees with (8) and evaluates its numerical coefficients.

§4. Monte Carlo Calculation of the PNG Transients

Let now show the Gilmer PNG model for the two-dimensional case of the crystal growth. He assumed that the clusters nucleate at random sites on the surface of the crystal and at a rate J per unit area, J is a fixed constant, independent of time and of the local surface structure. The clusters start with a radial speed v that is independent of radius. The appropriate vertical position for each event is determined by a comparison with previous events to calculate the height of the surface at that point. Periodic boundary conditions are employed to eliminate edge effects.

He chose the parameter describing the process in such a way that the results closely approximate those in the infinite system. If the linear dimension of the section is L, it is sufficient that $2v/L \ll JL^2$, i. e., the time required for a cluster to cover the surface is much larger than the average time between nucleation events. Gilmer took the value $v=2\times10^{-3}JL^3$, and with this choice approximately fifty nucleation events are generated as pairs of random number (x, y) in the interval between 0 and 1. The time between events is calculated with a third such random number z_t, using the relation

$$\Delta t=-\ln(z_t)/JL^2. \tag{33}$$

This method produces values of Δt that satisfy a Poisson distribution with an average value of $(JL^2)^{-1}$. The average growth rates measured at intervals during the depositions of the first four layers are shown in Fig. 1. The oscillations are no longer distinguishable after about four layers have been deposited, but the growth rate is still increasing slightly.

§5. Our Results of MC Simulations

We made the MC simulation for one and two dimensional cases of the crystal growth with several values of parameters. We made the simulation on the graphic screen for two dimensional case, visually. This method was very useful to determine whether the nucleation events is located on the new step or not. Since the main procedure is almost same as one made by Gilmer for two-dimensional case, then we describe the one dimensional case, in detail. The procedure of the MC calculation is as follows. We assume that the substrate has a finite line length of L. Then it is necessary to choose the parameters describing the system in such a way that the results are applicable as much as possible to an infinite system. We assume that the nucleation takes place at a rate J per unit length per unit time, where J is a fixed constant, independent of time and the local surface structure. The steps move after nucleation with speed v, which is assumed to be a constant. Then the time required for the steps to move to the boundary is $t_1=L/2v$, and the average time interval during the successive nucleation is $t_2=1/JL$. It is evident that if $t_1 \ll t_2$, the growth of a layer will be completed before the next nucleation event. It is convenient to introduce the dimensionless parameter a as $2a=t_2/t_1=2v/JL^2$. Therefore the condition $2a \ll 1$ corresponds to the case of the frequent nucleation events and the long line length of L. At the time interval of t_2, steps move as $\Delta L=vt_2=La$. In order to discuss the general process, we normalize the time by $t_0=(Jv)^{-1/2}$, and the

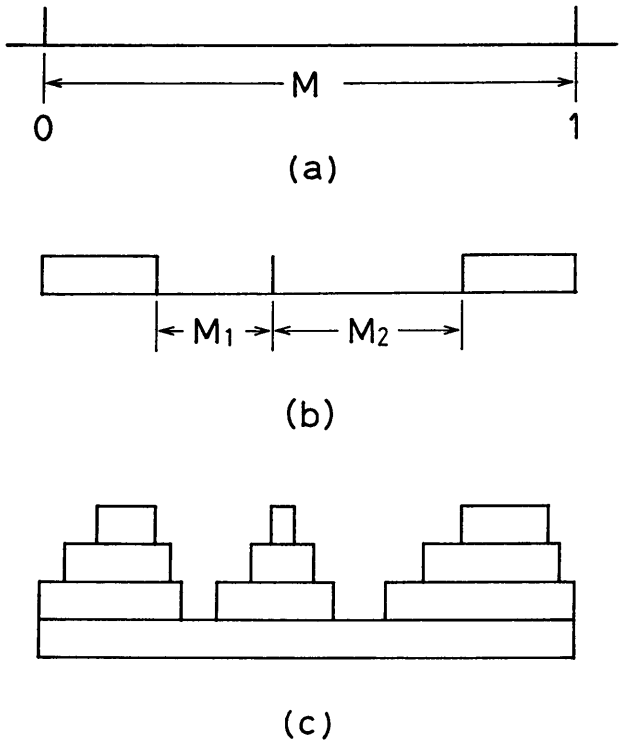

Fig. 2 (a) Schematic diagram of the segment with the periodic boundary conditions. (b) The subsegments after time interval of t. (c) A typical growth front of the crystal surface.

length by L. So we may describe the process by making use of the single parameter a as follows ; that is, the nucleation occurs at the average time interval of a, and the steps move with the velocity $\sqrt{a}\,(=t_0 v/L)$. In other words, it moves by a at the time interval of $\sqrt{a}$.

In actual simulation we take the line segment of unit length labeled by M with the periodic boundary condition. We assume that there exist only one nucleus on the substrate at the initial moment. The nucleation events are generated by a random number between 0 and 1, because it is assumed that the line segment has a unit length. The time between events is calculated with the random number N, using the relation

$$\Delta t = -\sqrt{a}\,\ln N. \qquad (34)$$

This method produces values of Δt that satisfy a Poisson distribution with an average of a. After the time Δt, the next nucleation events happen at anywhere on the line segment. Then we divide the segment M into two subsegments M_1 and M_2 as shown in Fig. 2. Thus the nucleation events are recorded in a list of the subdivided segments ; $M_i(n)$,

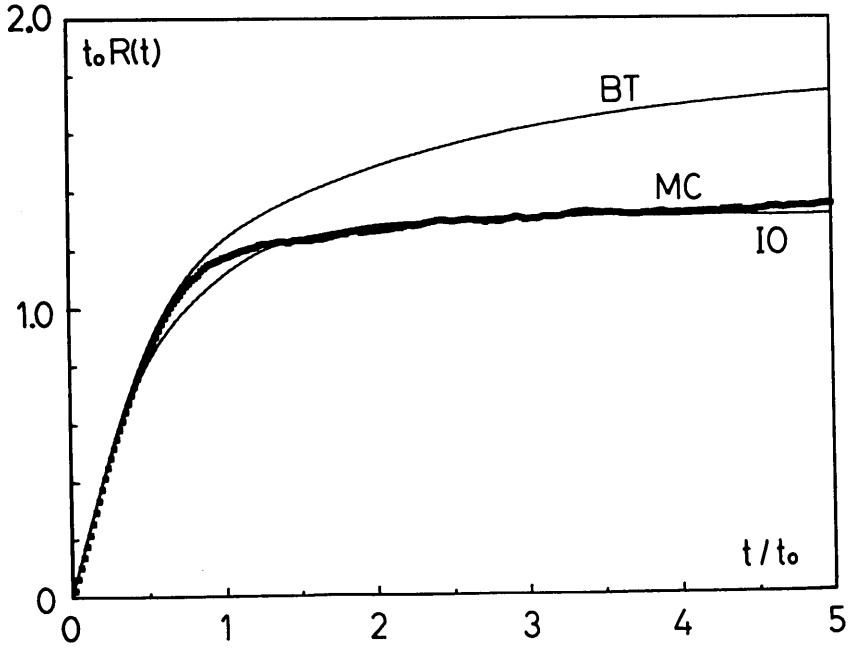

Fig. 3 The growth rate Rt_0 in the one dimensional case.

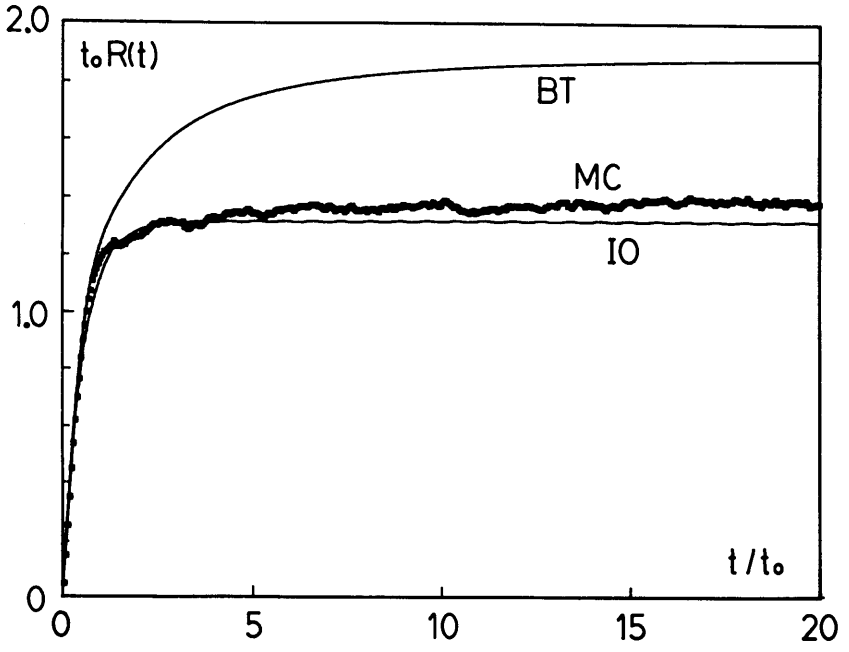

Fig. 4 The growth rate for the long simulation time of t/t_0.

which is the i-th subsegments in the n-th layer. The nucleation position of each new event is compared with one for previous events to determine whether the step from the earlier events has expanded to cover the point. We divide the segment into the subsegments $M_i(n)$ after the time interval Δt. This is a simple way to avoid examing the complicated phenomena of the coalescences of steps. Therefore the number of the steps in the n-th layer $c_n(t)$ is determined by the subtraction of the sum of the subsegments $M_i(n)$ from 1. Then the growth rate $R(t)=dc_n(t)/dt$ is calculated from each $c_n(t)$. The MC simulation were repeated 250 times. Average growth rate R for the case of $a=0.0001$ is shown in Fig. 3.

§6. Discussion

Now let us show the theoretical model given by Goldenfeld, which gives the same result discussed in §2. He got the exact solution of the one dimensional case or the finite system, which is written as[3]

$$Rt_0 = \sqrt{2}\, I(z), \tag{35}$$

where the dimensionless parameter z is given by

$$z = \sqrt{2/a}. \tag{36}$$

The function $I(z)$ possesses the limits

$$I(z) = \begin{cases} 1 - 1/2z + O(1/z^2) & z \gg 1 \quad (37) \\ (1/2)z(1 - z^2/8 + O(z^4)). & z \ll 1 \quad (38) \end{cases}$$

Then we get two solutions as the limit corresponding

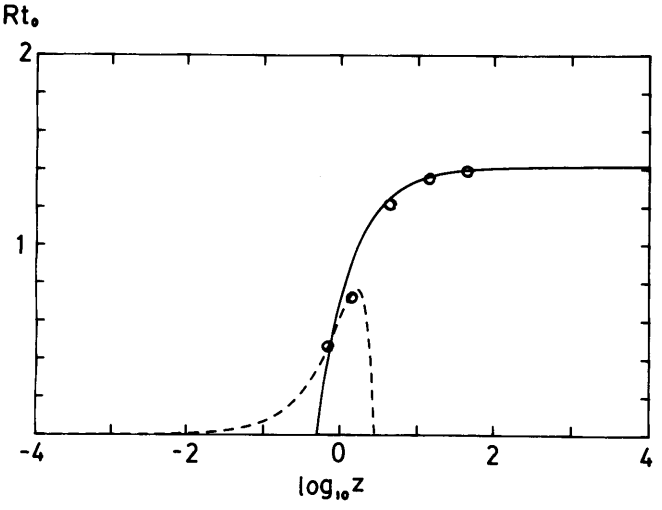

Fig. 5 MC simulations for several values of parameter z (shown by circles). The curves are plots of eqs. (37) and (38).

to eqs. (37) and (38) as

$$R t_0 = \sqrt{2} \tag{39}$$

and

$$R t_0 = 1 / \sqrt{a} . \tag{40}$$

Our result of the MC simulation is compared with eq. (39), because we treated the infinite system. The result of Borvinski-Tindergozen (BT) model[14], and Ishibashi-Orihara (IO) model[10,11] are also shown in Fig. 3.

Our MC results till the time $t/t_0 = 5$ seems to be support the IO model, which was inconsistent about 7% with the exact solution of $R t_0 = \sqrt{2}$. As above mentioned, our results are applicable to the infinite system, then it is expected that $R t_0$ becomes $\sqrt{2}$ at the stationary state. In order to check this point, we made the calculation for a long time till $t/t_0 = 20$. We got the closer value of 1.37 to 1.39 as $R t_0$, which is 2% lesser than the exact solution given by eq. (39) (Fig. 4.). It seems to be a good agreement with the exact solution (39). Moreover it is worthwhile to mention that our MC simulation results of $R t_0$ show the quicker transient to the stationary state than the IO model. We calculate the MC simulation for several values of parameter z. The results of our MC calculation are shown in Fig. 5. It shows the good agreement with the theoretical values which are given by (37) and (38).

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