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Growth and Decrescence of Two-Dimensional Crystals: A Markov Rate Process

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A Markov rate process whose transitions are captures and escapes of single atoms from the edge of a two-dimensional crystal is introduced. The stochastic equilibrium states of this process describe steady crystal growth, crystal–fluid equilibrium, and steady crystal decrescence. Exact and asymptotic growth rates are found. This extends recent results which dealt only with capture events. One application is to the growth of lamellar crystals from polymers.

KEY WORDS: Crystal growth; polymer crystals; Markov rate process; reversibility; dynamic reversibility; nonequilibrium statistical mechanics; solid-on-solid model.

1. INTRODUCTION

Recently Gates and Westcott[3,4] (henceforth referred to as GWI, GWII) showed how to analyze the steady growth of two-dimensional crystals using a Markov rate process whose states are representations of an edge of a crystal. When net growth occurs, the process is not reversible and most such nonreversible processes have proved mathematically intractable. In our case, however, we found that a property called *dynamic reversibility* held, and this enabled equilibrium distributions to be found. Stationary states of our process can then describe steady, positive growth. (I shall refer to these stationary states as equilibrium states, the equilibrium referring to the shape of the edge, not to an equilibrium between crystal and fluid phases.) The resulting growth rates give an exact and more detailed description of crystal growth at the molecular scale than was previously possible.

These results were applied in GWII to the analysis of growth regimes

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for lamellar crystals formed by polymers. Other possible applications are to growth of adsorbed layers on crystal surfaces, growth of edges on crystal surfaces due to dislocations, and growth of various cellular structures.

A limitation of this analysis is that it did not admit events in which *atoms* (or polymer chain segments or cells, etc.) escape from the crystal edge. Such events are more important when crystal growth is slow. They are essential for a description of the equilibrium between crystal and fluid phase. Here I show how to include such escape events in a Markov rate model. Given certain restrictions on the rates of capture and escape, one can give exact results for a continuum of steady states from rapid growth, through the two-phase equilibrium to rapid decrescence (which might occur by dissolving, melting, or vaporizing of the crystal edge).

I give processes that are appropriate for both hexagonal and square crystal structures. One can therefore provide exact treatments of a range of growth regimes and growth habits for crystals in two dimensions. The results supplement the extensive physical and chemical literature on the subject (e.g., refs. 10 and 11, and references cited). In some cases our results differ (Section 4 and GWI and GWII) from those derived by more physically based arguments.

This range of useful results in two dimensions seems not to extend easily to the process of three-dimensional crystal growth driven by nucleation (e.g., ref. 5). In three dimensions, one does not yet have even a probability distribution describing the surface of a growing crystal. (The well known distribution of Jackson,[8] the "SOS distribution," applies only to two-phase equilibrium, hence zero growth rate.) Three dimensional growth has been studied instead by computer simulation and by various ingenious approximations.[5,6]

2. MICROSCOPIC MODEL

Consider first the edge of a hexagonally structured crystal as illustrated in Fig. 1a, where *atoms* are represented by disks. Figure 1b illustrates events whereby *atoms* join or leave the edge with rates α, β, γ and α', β', γ', respectively.

Construct states in the manner of GWI by connecting the centers of edge disks as illustrated in Fig. 2. Labeling the line segments between centers by $+1$ for inclines, as one goes from left to right, and -1 for decines, one can represent the edge by the vector $\boldsymbol{\sigma} = (\sigma_1,..., \sigma_{2M})$, where $\sigma_i = 1, -1$. Impose periodic boundary conditions, $\sigma_{2M+i} = \sigma_i$, and the initial condition

$$\sum_{1}^{2M} \sigma_i = 0 \tag{2.1}$$

(a)

(b)

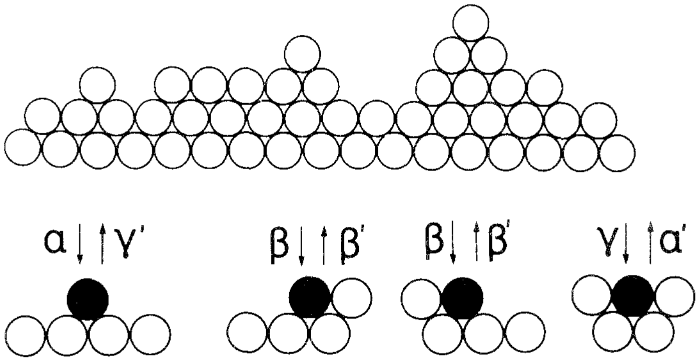

Fig. 1. (a) Edge of a crystal with hexagonal structure. (b) Single-atom transitions into and out of the crystal edge.

which gives the edge the same height at both ends. The events shown in Fig. 2b are all of the form

$$(\ldots, 1, -1, \ldots) \to (\ldots, -1, 1, \ldots)$$

or

$$(\ldots, -1, 1, \ldots) \to (\ldots, 1, -1, \ldots)$$

so that (2.1) holds for all time.

Suppose that the events shown in Fig. 1b occur according to a continuous-time Markov process with the transition probability rates α, β, γ and α', β', γ' between states $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}'$ say, and denote these in general by $q(\boldsymbol{\sigma}, \boldsymbol{\sigma}')$. This process is evidently irreducible and, since it has a finite state space, it is positive recurrent and must have a unique equilibrium

(a)

(b)

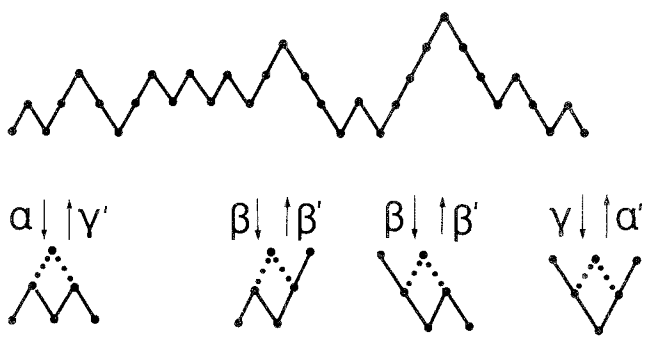

Fig. 2. (a) Representation of the crystal edge of Fig. 1a. (b) Representations of the transitions in Fig. 1b.

probability distribution $p(\boldsymbol{\sigma})$ which is always attained as time $t \to \infty$ in the process.

In general we cannot find $p(\boldsymbol{\sigma})$. We can, however, find it and the associated growth rate under the conditions

$$\alpha + \gamma = 2\beta \tag{2.2}$$

and

$$\alpha'/\alpha = \beta'/\beta = \gamma'/\gamma \tag{2.3}$$

The first of these arose in GWI. The new conditions imply that

$$\alpha' + \gamma' = 2\beta' \tag{2.4}$$

also. The three equality constraints leave three independent parameters, which I take as α, v, and η, where

$$\begin{aligned} &\beta = \alpha + v, \qquad \gamma = \alpha + 2v \\ &\alpha' = \eta\alpha, \qquad \beta' = \eta(\alpha + v), \qquad \gamma' = \eta(\alpha + 2v) \end{aligned} \tag{2.5}$$

As described in GWI, α can be interpreted as a nucleation rate (in the general sense) and v as an extension rate which describes the horizontal rate of extension of an incomplete layer of disks. The new parameter η relates the escape and capture rates in a curious way.

When growth is rapid, η will be relatively small; $\eta \ll 1$. When the crystal edge grows while remaining fairly flat (producing a crystal *facet*), α will be small compared to v. Thus, α', for the event where an atom escapes from a complete layer, will be nearly negligible. This latter event is sometimes given zero rate in growth studies (e.g., ref. 10). In our case, however, we cannot depart from (2.5) if we require exact solutions.

When $\eta = 1$, we shall find a condition of *detailed balance* (see Whittle[13] for a mathematical formulation) between escape and capture events and the process is *reversible*. It gives no net growth, but describes the two-phase equilibrium between crystal and fluid. When $\eta > 1$, we find a net decrescence or negative growth rate.

If we reparametrize (2.5) more symmetrically, but with a redundant parameter,

$$\begin{aligned} &\alpha = \lambda\alpha_0, \qquad \beta = \lambda(\alpha_0 + v_0), \qquad \gamma = \lambda(\alpha_0 + 2v_0) \\ &\alpha' = \lambda'\alpha_0, \qquad \beta = \lambda'(\alpha_0 + v_0), \qquad \gamma' = \lambda'(\alpha_0 + 2v_0) \end{aligned} \tag{2.6}$$

with $\lambda \geqslant 0$ and $\lambda' \geqslant 0$, then $\lambda' = 0$ gives no escape events, and $\lambda = 0$ gives no capture events, while

$\lambda' < \lambda$	gives net crystal growth
$\lambda' = \lambda$	gives two-phase equilibrium
$\lambda' > \lambda$	gives net crystal decrescence

The special case $\lambda = \lambda'$ gives a *reversible* process, and in general we shall find that the process is *dynamically reversible.* These parameters are functions of temperature and concentration, but this is not discussed further here (see refs. 5, 6, 8, 10, and 11).

3. THE STEADY STATE

We need to find the equilibrium distribution of our process, describing states where steady growth or steady decrescence occurs. Let $q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}')$ denote the transition rate matrix when $\eta = 0$. This is written out explicitly in several ways in Sections 2 and 3 of GWI, but its physical interpretation and its mathematical form are fairly clear from Fig. 2b. I now claim that the new process, with rates given by (2.5), has transition matrix

$$q(\boldsymbol{\sigma}, \boldsymbol{\sigma}') = q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}') + \eta q^0(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}') \tag{3.1}$$

To see this, note that $q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}')$ has value α when the transition $\boldsymbol{\sigma} \to \boldsymbol{\sigma}'$ has the form (recalling the periodic boundary conditions)

$$(..., 1, -1, 1, -1, ...) \to (..., 1, 1, -1, -1, ...) \tag{3.2a}$$

where the σ_i not shown remain unchanged. Hence $\eta q^0(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}')$ has the value $\eta\alpha = \alpha'$ when $\boldsymbol{\sigma} \to \boldsymbol{\sigma}'$ has the form

$$(..., -1, 1, -1, 1, ...) \to (..., -1, -1, 1, 1, ...) \tag{3.2b}$$

and this is the α' transition shown in Fig. 2b. Since $q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}') = 0$ for the transition (3.2b), we see that (3.1) is correct for the α and α' transitions. The transitions with rates β' and γ' may be checked against (3.1) in similar fashion, using the general property

$$q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}')\, q^0(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}') = 0 \qquad \text{for all } \boldsymbol{\sigma}, \boldsymbol{\sigma}' \tag{3.3}$$

In GWI we showed that the process with transition matrix q^0 is *dynamically reversible.* For present purposes one need note only that this implies that the equilibrium probability distribution $p^0(\boldsymbol{\sigma})$ satisfies the conditions[12,13]

$$p^0(\boldsymbol{\sigma}) = p^0(-\boldsymbol{\sigma}) \tag{3.4}$$

and

$$p^0(\boldsymbol{\sigma}')q^0(\boldsymbol{\sigma}', \boldsymbol{\sigma}) = p^0(\boldsymbol{\sigma})q^0(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}') \tag{3.5}$$

furthermore,

$$q^0(\boldsymbol{\sigma}) = q^0(-\boldsymbol{\sigma}) \tag{3.6}$$

where

$$q^0(\boldsymbol{\sigma}) = \sum_{\boldsymbol{\sigma}'} q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}') \tag{3.7}$$

these conditions holding for all $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}'$. Equation (3.5) is a modified form of the condition of *detailed balance* satisfied by classical reversible processes. The method now hinges on the following simple result, which seems to be new.

Proposition 1. For any dynamically reversible process with transition matrix q^0, the derived process with transition matrix of form (3.1) is dynamically reversible and has the same equilibrium distribution for all $\eta \geqslant 0$. For $\eta = 1$ the derived process is also reversible.

Proof. Replacing $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}'$ by $-\boldsymbol{\sigma}$ and $-\boldsymbol{\sigma}'$ in (3.5) and using (3.4) gives

$$p^0(\boldsymbol{\sigma}')q^0(-\boldsymbol{\sigma}', -\boldsymbol{\sigma}) = p^0(\boldsymbol{\sigma})q^0(\boldsymbol{\sigma}, \boldsymbol{\sigma}') \tag{3.8}$$

Adding (3.5) to η times (3.8) gives

$$p^0(\boldsymbol{\sigma}')q(\boldsymbol{\sigma}', \boldsymbol{\sigma}) = p^0(\boldsymbol{\sigma})\, q(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}') \tag{3.9}$$

Now putting

$$q(\boldsymbol{\sigma}) = \sum_{\boldsymbol{\sigma}'} q(\boldsymbol{\sigma}, \boldsymbol{\sigma}') \tag{3.10}$$

gives

$$\begin{aligned} q(-\boldsymbol{\sigma}) &= q^0(-\boldsymbol{\sigma}) + \eta q^0(\boldsymbol{\sigma}) \qquad [\text{by } (3.1)] \\ &= q^0(\boldsymbol{\sigma}) + \eta q^0(-\boldsymbol{\sigma}) \qquad [\text{by } (3.6)] \\ &= q(\boldsymbol{\sigma}) \end{aligned} \tag{3.11}$$

Equations (3.9) and (3.11) verify the conditions corresponding to (3.5) and (3.6) for dynamic reversibility of the derived process, and (3.9) identifies p^0 as its equilibrium distribution. Further, from (3.1)

$$q(-\boldsymbol{\sigma}, -\boldsymbol{\sigma}') = q(\boldsymbol{\sigma}, \boldsymbol{\sigma}') \qquad \text{if} \quad \eta = 1$$

so that (3.5) reduces to the standard condition of detailed balance, showing the process to be reversible (e.g., ref. 13). This proves the proposition. (Note that the proposition holds for σ_i taking any sets of values, and $-\boldsymbol{\sigma}$ representing any operation on $\boldsymbol{\sigma}$, defining a set of conjugate states in the manner of Whittle.[12,13])

Returning to the process of interest, we have from GWI

$$p^0(\boldsymbol{\sigma}) = Z^{-1} \exp\left(-J \sum^{N} \sigma_i \sigma_{i+1}\right) \qquad \text{and} \qquad \sum_{i=1}^{N} \sigma_i = 0 \tag{3.12}$$

where

$$J = \tfrac{1}{4} \log(\gamma/\alpha) > 0 \tag{3.13}$$

and Z is a normalizing constant and, by Proposition 1, this is the equilibrium distribution of our general process for any $\eta \geqslant 0$ and rates satisfying (2.5).

Define the growth rate as the rate of change of the expected number of atoms in the crystal per unit atomic distance along the edge. By the argument of GWI, the steady-state growth rate is

$$\begin{aligned} G &= [\langle q^0(\boldsymbol{\sigma})\rangle - \eta \langle q^0(-\boldsymbol{\sigma})\rangle]/M \\ &= (1-\eta)\langle q^0(\boldsymbol{\sigma})\rangle/M \\ &= (1-\eta) G^0 \end{aligned} \tag{3.14}$$

by (3.6), where the expectation $\langle \cdot \rangle$ is with respect to p^0, and G^0 is the growth rate when $\eta = 0$.

From the form of p^0 and q^0 it follows that, for fixed M, we can write

$$G^0 = \alpha f(\alpha/\gamma) \tag{3.15}$$

for some function f. Putting, for $\eta < 1$,

$$\bar{\alpha} = \alpha - \alpha' \qquad \text{and} \qquad \bar{\gamma} = \gamma - \gamma' \tag{3.16}$$

which represent, in a perverse sense, net rates for α and γ events, we obtain from (3.14)

$$G = \bar{\alpha} f(\bar{\alpha}/\bar{\gamma}) \tag{3.17}$$

which is just the growth rate for a process with capture events only, of rates $\bar{\alpha}$, $\bar{\gamma}$, and $\bar{\beta} = (\bar{\alpha} + \bar{\gamma})/2$. This process evidently has the same equilibrium distribution p^0 as well.

In GWII we evaluated G^0 exactly and in various limiting regimes. For example, for fixed α and v, and $M \to \infty$ we found

$$G^0 \to (\alpha\gamma)^{1/2}/[1 + (\alpha/\gamma)^{1/2}] \tag{3.18}$$

which, with (3.14), gives the limiting form of G in this long-edge limit.

4. SQUARE CRYSTAL STRUCTURE

Here the edge of a crystal is the upper profile of vertical stacks or columns of squares as illustrated in Fig. 3a. Figure 3b illustrates the capture and escape events with rates α, β, γ, and α', β', γ' again.

States of the process are vectors $\mathbf{h} = (h_1, ..., h_M)$, where the h_i are integers (positive or negative) representing the size of the up steps when moving from left to right along the crystal edge ($h_i = 0$ means no step, $h_i < 0$ means a down step). Equal heights at the ends implies

$$\sum_1^M h_i = 0 \tag{4.1}$$

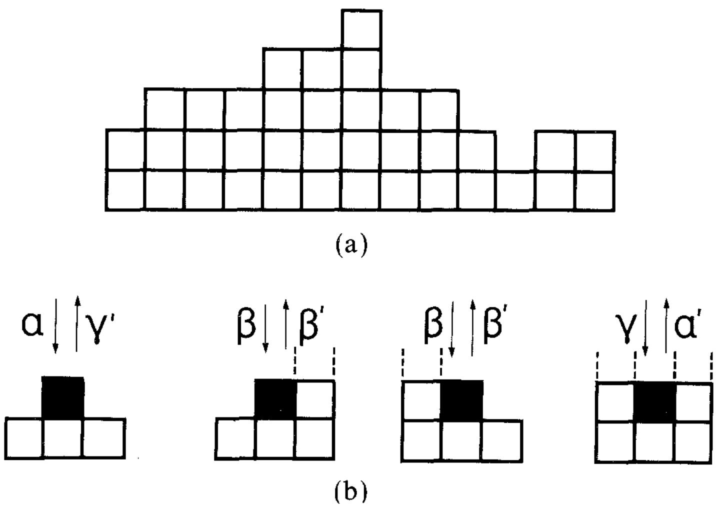

Fig. 3. (a) Edge of a crystal with square structure. (b) Single-atom transitions into and out of the crystal edge. The presence of further side neighbor atoms, indicated by dashed lines, does not influence these rates. Atoms can leave the top site or add to the top site of any column.

which is evidently preserved by the transitions. Again I assume a continuous-time Markov process with transition probability rates indicated in Fig. 3b and denoted in general by $q(\mathbf{h}, \mathbf{h}')$. Irreducibility of this process does *not* guarantee existence of an equilibrium probability $p(\mathbf{h})$. The process may be null recurrent or transient.

Again one can find $p(\mathbf{h})$ only in the case where the rates satisfy (2.2) and (2.3), or equivalently (2.5). I claim that

$$q(\mathbf{h}, \mathbf{h}') = q^0(\mathbf{h}, \mathbf{h}') + \eta q^0(-\mathbf{h}, -\mathbf{h}') \tag{4.2}$$

where q^0 corresponds to the process with $\eta = 0$. Checking this, note from Fig. 3b that $q^0(\mathbf{h}, \mathbf{h}')$ has value α when the transition $\mathbf{h} \to \mathbf{h}'$ has the form (taking $h_{M+1} = h_1$)

$$\begin{aligned} h_j \geqslant 0 &\to h_j + 1 \\ h_{j+1} \leqslant 0 &\to h_{j+1} - 1 \end{aligned} \tag{4.3}$$

with the other h_i unchanged. Thus, $\eta q^0(-\mathbf{h}, -\mathbf{h}')$ has the value $\eta\alpha = \alpha'$ when $\mathbf{h} \to \mathbf{h}'$ has the form

$$\begin{aligned} h_j \leqslant 0 &\to h_j - 1 \\ h_{j+1} \geqslant 0 &\to h_{j+1} + 1 \end{aligned} \tag{4.4}$$

This agrees with the α' transition in Fig. 3b. Noting that

$$q^0(\mathbf{h}, \mathbf{h}') q^0(-\mathbf{h}, -\mathbf{h}') = 0 \tag{4.5}$$

and checking other transitions in a similar way confirms (4.2).

In GWI we showed this $\eta = 0$ process to be dynamically reversible, giving equations like (3.4)–(3.7). Thus, by the arguments of Section 3, the process is dynamically reversible for all $\eta \geqslant 0$. The equilibrium distribution is, for all $\eta \geqslant 0$ and $\nu > 0$,

$$p^0(\mathbf{h}) = Z^{-1} \exp\left(-2J \sum_1^M |h_i|\right), \qquad \sum_1^N h_i = 0 \tag{4.6}$$

with J as in (3.13) and Z a (new) normalizing constant. The results (3.14)–(3.17) are again applicable, and from GWII

$$G^0 \to (\alpha\gamma)^{1/2} \qquad \text{as} \quad M \to \infty \tag{4.7}$$

whence

$$G \to (\alpha\gamma)^{1/2} (1 - \eta) = G_\infty, \quad \text{say,} \qquad \text{as} \quad M \to \infty \tag{4.8}$$

Sadler [ref. 10, Eq. (12)] reviews a more physically based argument, giving in the present notation, a growth rate

$$G_p = (2\alpha\beta)^{1/2}\,(1-\beta'/\beta) \tag{4.9}$$

He does not use conditions (2.2) and (2.3), but takes instead

$$\gamma' = \beta' \qquad \text{and} \qquad \alpha' = 0 \tag{4.10}$$

To compare (4.8) with (4.9), choose α, β, γ, α', β', and γ' satisfying (2.2) and (2.3), giving

$$G_\infty = [\alpha(2\beta-\alpha)]^{1/2}\,(1-\beta'/\beta) \tag{4.11}$$

Now hold α, β, γ, and β' fixed and reduce α' and γ' so that (4.10) is satisfied. Reducing some escape rates, other rates remaining constant, increases the growth rate. So a Markov process would predict a growth rate greater than (4.11) under Sadler's conditions, a result not inconsistent with G_p.

When $\alpha \ll v$, whence $\alpha \ll 2\beta$, as is common for polymer crystallization, (4.9) and (4.11) are very close. This, however, is the case where (4.10) and (2.4) are most at odds.

Most notably, G_p and G_∞ definitely disagree when $\alpha=\beta=\gamma\neq 0$ and $\alpha'=\beta'=\gamma'=0$, giving values $2^{1/2}\alpha$ and α, respectively. Sadler[10] already noted a dilemma created by this factor of $2^{1/2}$ in G_p.

Rates other than (2.5) with $\eta=1$ can be chosen to give reversible processes with equilibrium distribution of the form (4.6) and describing the two-phase equilibrium (e.g., the two-dimensional version of the process of Jackson[8]). Such processes, however, when modified so as to give net crystal growth (e.g., Refs. 5 and 6), seem not to be amenable to exact analysis.

In GWI (Section 12) we showed how the edge roughness of the crystal was quantified in a natural way by the diffusion coefficient

$$2(\alpha/\gamma)^{1/2}/[1-(\alpha/\gamma)^{1/2}]$$

of a random walker whose steps are the h_i. This result is independent of η, a consequence of the fact that the equilibrium distribution (4.6) is independent of η. Physically this means roughly that the γ' events, which tend to remove nucleations and produce a smoother edge, are balanced by the β' transitions, which slow the extension of layers and so tend to produce a rougher edge. Similar considerations apply to the hexagonal crystal structure (GWI, Section 12).

5. CONTINUUM LIMIT

In GWI we gave a rigorous argument concerning the convergence of the $\eta = 0$ Markov processes to a continuous state-space process studied most recently by Bennett *et al.*[1] and Goldenfeld.[7] Rather than extending this lengthy argument to $\eta \geqslant 0$, I give a more heuristic version. Fix η and take

$$\alpha = iL/M \qquad \text{and} \qquad v = gM/L \tag{5.1}$$

for fixed $i > 0$, $g > 0$, and $L > 0$, with other rates given by (2.5). For either the square or hexagonal model, take a complete layer of M atoms partly covered by a single incomplete layer (of $M/2$ atoms, say). By (5.1), α and α' transitions are very rare as $M \to \infty$. If there are none in $(0, t)$, then there are no γ or γ' transitions either (a.s. as $M \to \infty$). Thus, the process comprises independent Poisson processes of rates β and β'. If we shrink atoms to width L/M, so that the edge has fixed length L, then a step advances a distance

$$X = (L/M)[N(t) - N'(t)]$$

in time t, where $N(t)$ and $N'(t)$ are the numbers of β and β' transitions in time t. Thus, X has mean

$$(L/M)(\beta - \beta')t \to g(1-\eta)t \qquad \text{as} \quad M \to \infty$$

by (5.1), and variance

$$(L^2/M^2)(\beta + \beta')t \to 0 \qquad \text{as} \quad M \to \infty$$

Thus, a step moves deterministically with speed $g(1-\eta)$ in the limit. If $\eta < 1$, layers become longer; if $\eta = 1$, they remain static; and if $\eta < 1$, they shrink to nothing.

Isolated nucleations on a complete layer occur at rate iL/M per *atomic* distance, hence at rate i per unit length. In GWI the process of all α transitions is shown for $\eta = 0$ to converge to a Poisson process of rate i uniform on the edge $[0, L]$ and on time intervals. For $\eta > 0$, there is no certainty that a nucleation (α event) will survive, so that the analysis in GWI does not carry straight over. To continue the heuristic argument, suppose a single nucleation has occurred on a single-layer configuration of length M sites. Henceforth, the only events of significant probability for large M are γ' transitions with probability

$$\gamma'/[\gamma' + 2\beta + (M-3)\alpha] \to \eta/(1+\eta) \qquad \text{as} \quad M \to \infty$$

β transitions with total probability

$$2\beta/[\gamma' + 2\beta + (M-3)\alpha] \to 1/(1+\eta) \qquad \text{as} \quad M \to \infty$$

if the new layer has length 1, and

$$2\beta/[2\beta' + 2\beta + (M-n-2)\alpha] \to 1/(1+\eta) \qquad \text{as} \quad M \to \infty$$

if the new layer has length n and $1 < n \leqslant M-2$, and β' transitions with total probability 0 if $n = 1$, and probability

$$2\beta'/[2\beta' + 2\beta + (M-n-2)\alpha] \to \eta/(1+\eta) \qquad \text{as} \quad M \to \infty$$

if $1 < n \leqslant M-2$. So, as $M \to \infty$, the probability of loss of the original nucleation is just the probability of ruin of a gambler with initial stake 1 and probability $p = 1/(1+\eta)$ of winning and $q = \eta/(1+\eta)$ of losing at each play (against an infinite bank). A classical result [ref. 2, p. 347, Eq. (2.8)] is that the gambler's ultimate ruin has probability

$$\begin{array}{ll} 1 & \text{if} \quad q > p, \text{ i.e., } \eta > 1 \\ q/p = \eta & \text{if} \quad q < p, \text{ i.e., } \eta < 1 \end{array}$$

Thus, the nucleation survives with probability $1-\eta$ if $\eta < 1$, and so its rate tends as $M \to \infty$ to an effective nucleation rate $(1-\eta)\alpha$. If $\eta > 1$, it does not survive. To be observed at all in the continuum limit it must extend to length at least λM for some $\lambda > 0$, which it does with probability $1/\lambda M$ if $\eta > 1$ [ref. 2, p. 345, Eq. (2.5)]. Thus, there are no nucleations in the continuum limit if $\eta > 1$. (Note the distinction between these ruin or random walk problems and those mentioned at the end of Section 4.)

Then the result of Bennett *et al.*[1] gives, for this continuum model, the growth rate

$$G_{\text{cont}} = [2i(1-\eta)\, g(1-\eta)]^{1/2}\, I_1(u)/I_0(u)$$

for $\eta < 1$, where

$$\begin{aligned} u &= L[2i(1-\eta)/g(1-\eta)]^{1/2} \\ &= L(2i/g)^{1/2} \end{aligned}$$

So we can write

$$G_{\text{cont}} = (1-\eta)\, G^0_{\text{cont}}$$

where G^0_{cont} is the result for $\eta = 0$. This latter result follows also from (3.14) and the direct proof that $G^0 \to G^0_{\text{cont}}$ given in GWII.

Finally, note that for $\eta = 1$, the reversible case, the continuum limit process is entirely static: There is no nucleation or extension. For $\eta > 1$, the limit process is a reversed version of the Bennett *et al.* model, where gaps are spontaneously created in layers, and these gaps grow deterministically.

6. FINAL COMMENT

For $\nu \leqslant 0$ one has well-defined processes provided $\alpha + 2\nu \geqslant 0$. For the square case, $Z = \infty$ in (4.6), so there is no equilibrium distribution (ref. 9, p. 3) and the process is not positive-recurrent. If $\alpha + 2\nu = 0$, whence $\gamma = 0$, the process is evidently transient. This shows that there is a fundamental physical difference in growth behavior between the cases $\alpha < \beta < \gamma$ and $\alpha > \beta > \gamma$. Since α, β, and γ vary with temperature and concentration in the fluid, this difference might be observable as a physical discontinuity. The latter case may be relevant to the dendritic growth habit sometimes observed.

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