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Initial evolution of Kashchiev models of thin-film growth

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Abstract. We consider a continuum model of thin-film growth on an infinite perfect substrate. Multilayers grow by random nucleation of islands, at fixed rate, followed by lateral expansion at constant speed. Our focus is on the evolution of the film profile in the regime of small thicknesses. We present results for the layer coverages, the interface width, and the Bragg intensity oscillations, obtained by numerical integration of the original Kashchiev recursion relations. Asymptotically, the model shows Kardar–Parisi–Zhang universality scaling. Expressions for spatial correlation functions are also developed.

1. Introduction

There has been much recent interest in irreversible models for far-from-equilibrium self-affine film growth [1–3]. Typical studies introduce stochastic lattice models [4], although a few continuum models have also been considered [4–6]. Generally, analytic solutions are rare even in one dimension (the substrate dimension). The primary interest is in the universal asymptotic behaviour of the interface width [4] (a measure of the number of incomplete layers), $w \approx L^{\alpha} f(t/L^{\alpha/\beta})$, for a system of size L, at time t. This scaling holds for epitaxial films [7], of interest here. The conventional scaling function has the form $f(x) \approx x^{\beta}$ for $x \ll 1$, and approaches a constant for $x \gg 1$, thus we have $w \sim L^{\alpha}$ as $t \to \infty$, and $w \sim t^{\beta}$ as $L \to \infty$, for large t. For deposition at non-normal incident fluxes, a generalized anisotropic scaling form for f has been developed [8]. A coarse-grained description of models by appropriate stochastic partial differential equations elucidates their assignment to a few universality classes with distinct values of α and β. These exponents depend only on a small set of local growth rules, besides the substrate dimensionality and the properties of the noise. We note however that often the short-time *transient* behaviour is of more experimental interest and relevance [9], although it is not usually addressed in the above studies. This will be the focus of the present work.

The Kashchiev or polynuclear growth (PNG) model, defined in arbitrary dimension, is the multilayer generalization [10, 11] of the submonolayer version introduced originally by Kolmogoroff [12] and Avrami [13] (see also Johnson and Mehl [14]). In its simplest formulation it involves the homogeneous time-independent nucleation of islands at random positions on each supported layer, starting with a smooth substrate, with subsequent isotropic island expansion at constant speed, satisfying a *no-overhang* condition. An island stops expanding when it contacts a neighbouring island in the same layer. The extension of the model to account for variable, system-specific nucleation and growth rates is straightforward [11]. As noted originally [11], the kinetics of a given layer, at a certain time, is unrelated to that of all layers above, but depends on the growth rate of the preceding layer at *all* earlier times. Non-trivial recursion relations between successive layer coverages can be developed and exploited in general [11].

The Kashchiev model [11] is also obtained as the strong clustering limit of certain multilayer cooperative filling processes on a lattice [15–16]. The lattice processes involve competition between nucleation and growth of Eden clusters in each layer. Growth is enhanced at island perimeter sites, by a factor $\sigma > 1$, say, relative to growth at sites with no occupied neighbours. In the limit as $\sigma \rightarrow \infty$, with suitable rescaling of the lattice spacing, this model reduces to that of Kashchiev. Exact analysis of this lattice model is only possible for the first layer and in one dimension [15, 16]. Similar models with an additional restricted solid-in-solid constraint have been considered [17]. They show Kardar–Parisi–Zhang [18] (KPZ) behaviour for large σ where they reduce to the Kashchiev model.

The Kashchiev model provides a simplified description of the kinetics of nucleation-mediated crystal formation on surfaces free of dislocations [11]. It is naturally well suited to describe layered systems, like polymer crystals [19] and electrodeposits [20]. The submonolyaer version has been associated [21–24] with the kinetics of metastable domain growth, having reproduced universal growth curves and grain-size distributions over a wide range of characteristic parameters. One should realize that the model (of random irreversible nucleation of immobile islands of negligible initial size, expanding radially at constant speed [12, 13]) is often over-simplistic in some of its assumptions. For instance, island dissolution and large critical radii are not uncommon and introduce an extra timescale [25] in the Kolmogoroff–Avrami formulation. However, many experimental situations in thin-film growth effectively correspond to a very small critical nucleus [26]. The assumption that the lateral island velocity is constant during growth holds only at large front curvatures [27], if at all, but variable speeds are not hard to incorporate in the model. Analogously, long-range correlations (e.g. associated with elastic forces) among islands have not been properly accounted for in any of the current applications of the model even in systems where nucleation is known to be driven by surface stress fields [23]. For the same reason, the model is not expected to perform well in the vicinity of critical points.

Both analytical and numerical studies of the Kashchiev model have been reported in the literature [11, 19, 20, 28–34]. They typically relate experimentally accessible quantities, e.g. the film growth rate, to the growth mode and the conditions of the film interface. All simulations confirm that a constant non-zero overall growth rate sets in after a few layers form. Rangarajan [28] derived an exact expression for this constant. Although circular island shapes are commonly chosen, the approach is not restrictive of the island shape. Oldfield [29] simulated the steady-state growth of aligned squares, assuming electro-deposition parameters typical of the formation of mercury salts on mercury. He addessed the oscillatory structure of current transients (thus the film roughness) in terms of the nucleation and lateral growth rates, or rather a combination thereof (see below). Clearly, the higher the nucleation rate at fixed lateral growth speed, the rougher the film interface, at any given time. His results for the growth rates do not reveal pronounced island shape effects. Gilmer's simulations [31] also focused on the asymptotic growth rate and the details of the initial transients. Kashchiev [11] allows for general kinetics of layer filling showing that closed-form solutions are possible for general nucleation and expansion rates. He has provided detailed exact expressions for these. His work focused on the average film height and the overall film growth rate, and provided the first clear understanding of the layer coverage recursion relations for the multilayer case. These we review in the next section.

For a *finite* one-dimensional substrate, the steady state of the Kashchiev or PNG model can be analysed exactly [19, 32, 33]. Here the film interface width saturates at a value that scales non-trivially with the system size. The analysis relies on the map between the dynamics of the PNG model and that of the harmonic Sine–Gordon chain [33], whose fluctuations behave as in a gas of kinks and antikinks. Kinks and antikinks are created randomly in pairs, say at rate r, move in opposite directions, with uniform speed u, and annihilate each other when they merge. Random variables describing kink (n_+) and antikink (n_-) densities satisfy $\partial n_\pm/\partial t = r - 2un_+n_- \pm u\nabla n_\pm$, the terms on the right corresponding to creation, annihilation and drift of the specific kink type, respectively [30, 32, 33]. Clearly $n_+ - n_-$ is conserved by the dynamics. A steady-state measure exists where $\partial\langle n_\pm\rangle/\partial t = 0$ and the kink densities are uniform, hence $\nabla\langle n_\pm\rangle = 0$, and the spatial correlations between kinks and antikinks (as well as between kinks) are identically zero [33]. Thus $\langle n_+n_-\rangle = \langle n_+\rangle\langle n_-\rangle$ and one obtains $r = 2u\langle n_+\rangle\langle n_-\rangle$. Simple algebra gives for the average steady-state kink flux, defined as $\langle J\rangle = u(\langle n_+\rangle + \langle n_-\rangle)$, the important relation $\langle J\rangle = [(\langle n_+\rangle - \langle n_-\rangle)^2 + 2r/u]^{1/2}$. It follows that, in the film growth equivalent, $\langle J\rangle$ gives the rate of increase of the average interface height h, whereas $\langle n_+\rangle - \langle n_-\rangle$ corresponds to the slope of the growing interface, ∇h. For $r \neq 0$ and sufficiently small gradients, one finds $\partial h/\partial t \sim (2ru)^{1/2} + (u^3/8r)^{1/2}(\nabla h)^2$. This implies that the model belongs to the KPZ universality class [18] (which has $\alpha = \frac{1}{2}$, $\beta = \frac{1}{3}$). Note that the coefficient in front of the nonlinearity is positive, indicating that the film growth is enhanced on tilted (stepped) substrates. This is intuitive given the preferential growth at kink positions.

The outline of the remaining of this work is as follows. We review the Kashchiev model in the next section. Numerical integration of the monolayer coverages, from Kashchiev's original recursion solutions [11], is described in section 3, and in section 4 we recall some common measures of film growth and roughness in terms of the layer coverages. We provide results for the transient behaviour of the growing film, and a brief scaling analysis of the asymptotic non-epitaxial regime, at late times. The latter is limited by the number of integrated monolayers. The behaviour of the multilayer spatial correlations in analysed in section 5. We summarize our results in section 6.

2. The model

Figure 1 is a schematic of the model in one dimension. One starts at $t = 0$ with an infinite perfect substrate on which a multilayer film grows. Islands nucleate at random in layer j, on top of islands in layer $j-1$, at average rate $r_j(t)$ at time t, per unit time and 'area'. Thereafter the islands expand laterally with speed $v_j(\delta t)$, which depends on the time interval δt since nucleation, developing into 'bricks' [19] in $d = 1$, disks in $d = 2$, etc. Here d denotes the substrate dimensionality. In general, r_j and v_j depend explicitly on time, but $v_j \geqslant v_{j+1}$ is necessary to avoid overhangs. Islands are immobile. The radial growth of an island stops when it meets with another expanding island. Simple dimensional analysis obtains characteristic time and length scales in the model, in terms of the rates r and v, namely $\tau_0 = (rv^d)^{-1/(d+1)}$ and $l_0 = (v/r)^{1/(d+1)}$.

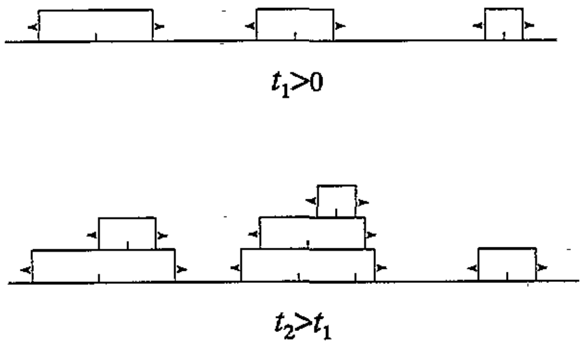


Figure 1. Two stages of growth in the Kashchiev model in one dimension. The ticks indicate the positions where the islands nucleated. Two islands at the centre of the lower diagram have already merged.

At some time $t>0$, a fraction $\theta_1(t)$ of the substrate is covered with the deposit. The general form of θ_1, due to Kolmogoroff [12] and Avrami [13], is

$$1-\theta_1(t)=\exp\left\{-c\int_0^t \mathrm{d}s\, r_1(s)\left[\int_s^t \mathrm{d}z\, v_1(z-s)\right]^d\right\} \tag{1}$$

where c is a constant reflecting the shape of the islands ($c=2$, π, $4\pi/3$, for disks in $d=1,2,3$). *The above expression results from considering in general [23] the necessary* and sufficient condition for any point of the substrate *not* to be covered with an island, at time t: no island can be nucleated at time $s\leqslant t$ within a distance $\int_s^t v_1(z-s)\,\mathrm{d}z$ of that point. Noting that the nucleation is a Poisson process, the exponential term is then simply the probability that such an island was *not* nucleated throughout the entire time interval, until time t. In the case when $r_1=r$ and $v_1=v$ are time independent, one obtains

$$\theta_1(t)=1-\exp\left[-\left(\frac{t}{\tau}\right)^{d+1}\right] \tag{2}$$

with $\tau=[(d+1)/c]^{1/(d+1)}\tau_0$.

Next we present Kashchiev's [11] recursion relations for higher layer coverages. We consider only the case where r_j and v_j are constant, with $v_j\geqslant v_{j+1}$. Generalization is straightforward (provided, e.g. $v_j(t)\geqslant v_{j+1}(t')$ for all t, t'). Suppose an infinitesimal portion $\mathrm{d}\theta_j(t')$ of layer j is created at time t'. The fraction of *this* newly created platform for islands in layer $j+1$ which is covered at time $t>t'$ simply equals the fraction of the substrate, in the submonolayer problem at the corresponding layer-$(j+1)$ nucleation and expansion rates [11], which is covered at time $t-t'$. Thus one has

$$\frac{\mathrm{d}\theta_{j+1}(t)}{\mathrm{d}\theta_j(t')}=1-\exp\left[-\left(\frac{t-t'}{\tau_{j+1}}\right)^{d+1}\right]. \tag{3}$$

One might naturally expect [34] that subsequent covering of points on the platform $\mathrm{d}\theta_j(t')$ would be affected by its finite size. However, for time $\bar{t}$ with $t'\leqslant\bar{t}\leqslant t$, points in layer j within a distance $(\bar{t}-t')v_j$ of the infinitesimal platform are necessarily filled by expansion of the platform, at speed v_j, or some other island. But the state of a point on top of the platform at time $\bar{t}$ can only be affected by the state of layer-j points within a distance $(\bar{t}-t')v_{j+1}$ from the platform (with $v_{j+1} \leqslant v_j$). Thus, as regards its subsequent covering, the platform is *effectively* infinite.

From (3) recursion relations between adjacent layer coverages can be built, at any time $t>0$. Assuming, for simplicity, that τ is layer independent, one has, for $j \geqslant 0$,

$$\theta_{j+1}(t) = \int_0^t \mathrm{d}t' \left\{ 1 - \exp\left[-\left(\frac{t-t'}{\tau} \right)^{d+1} \right] \right\} \frac{\mathrm{d}\theta_j(t')}{\mathrm{d}t'} \tag{4}$$

with $\theta_{j\geqslant 1}(0)=0$, and $\theta_0(t)=1$, $\mathrm{d}\theta_0/\mathrm{d}t=\delta(t)$, the Dirac delta function.

3. The layer coverages: numerical analysis

The recursion relations in (4) are easy to integrate numerically, in one of several forms, though evaluation of higher-layer coverages rapidly becomes computationally expensive. We used the form

$$\theta_{j+1}(t) = \frac{d+1}{\tau} \int_0^t \mathrm{d}t' \left(\frac{t-t'}{\tau} \right)^d \exp\left[-\left(\frac{t-t'}{\tau} \right)^{d+1} \right] \theta_j(t') \qquad j \geqslant 0 \tag{5}$$

(which results from (4) after integrating once by parts, and fixing $\tau_{j\geqslant 1}=\tau$), to obtain several layer coverages in one and two dimensions, with the choice $\tau=2$. Since τ sets the only timescale in the model, this choice is clearly arbitrary, as long as it is finite. Figure 2 shows the evolution of these layer coverages in time. Note how the number of incomplete layers, at a given time, decreases with d and, for each d, increases as the film grows. A reliable numerical treatment of the asymptotic (large-t) regime requires evaluation of far more layers, impractical on a Silicon Graphics machine. We have also performed calculations (not reproduced here) using simple approximation schemes, as suggested by Kashchiev [11]. These basically rely on the fact that the exponential function that enters in (5), or its derivative, are asymptotically sharply peaked around $t' \approx t$, for $t \gg \tau$. One is then naturally inclined to adopt simplified expressions, like $\theta_{j+1}(t) \approx \theta_j(t) \int_0^t \mathrm{d}/\mathrm{d}t' \{\exp\{-[(t-t')/\tau]^{d+1}\}\} \,\mathrm{d}t' \approx \theta_1 \theta_j$, for $j \geqslant 0$. We find that these approximations rapidly loose quality as one advances to higher layers.

4. Measures of film growth and roughness

In terms of the monolayer coverages, $\theta_{j\geqslant 0}$, the net fraction of the surface exposed in layer j is the difference $N_{j\geqslant 1}(t) = \theta_{j-1}(t) - \theta_j(t) \geqslant 0$, given the absence of overhangs. Note that $\Sigma_j N_j = 1$. The average film height, $h=h(t)$, or total coverage, is then simply†

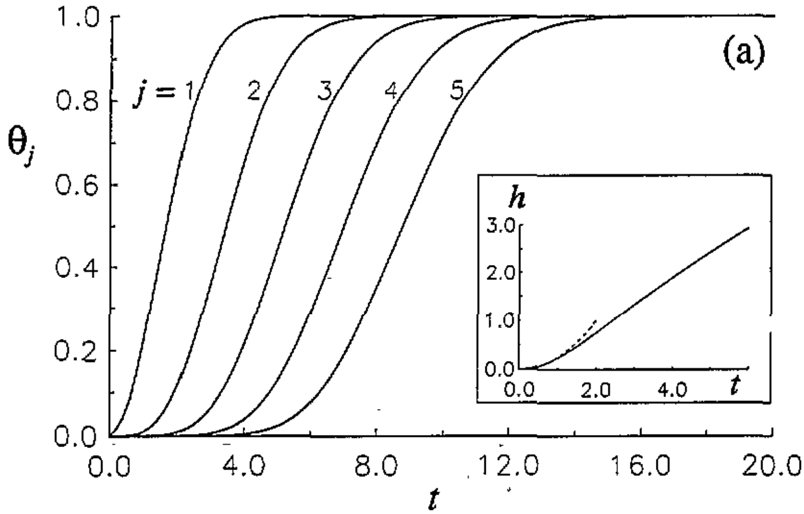
$$h(t) = \sum_{j=1}^{\infty} jN_j(t) = \sum_{j=1}^{\infty} \theta_j(t) \tag{6}$$

which, using (4), satisfies

$$\int_0^t \mathrm{d}t' \exp\left[-\left(\frac{t-t'}{\tau} \right)^{d+1} \right] \frac{\mathrm{d}h(t')}{\mathrm{d}t'} = 1 - \exp\left[-\left(\frac{t}{\tau} \right)^{d+1} \right]. \tag{7}$$

In the insets of figure 2 we illustrate the behaviour of h in time. The approach to the asymptotic linear regime takes less than two layers. Assuming $h(t) \sim U_\infty t$, as $t \to \infty$, and substituting into (7), yields in this limit $U_\infty = 1/\int_0^\infty \exp[-(u/\tau)^{d+1}]\,\mathrm{d}u$. On the other hand, one finds that $h(t\to 0) \sim (t/\tau)^{d+1}$.

† In general, $\sum_{j\geqslant 1} j^m N_j = \sum_{j\geqslant 0} [(j+1)^m - j^m]\theta_j = \sum_{j\geqslant 0} \sum_{0\leqslant k<m} \binom{m}{k} j^k \theta_j$, for $m \geqslant 0$.



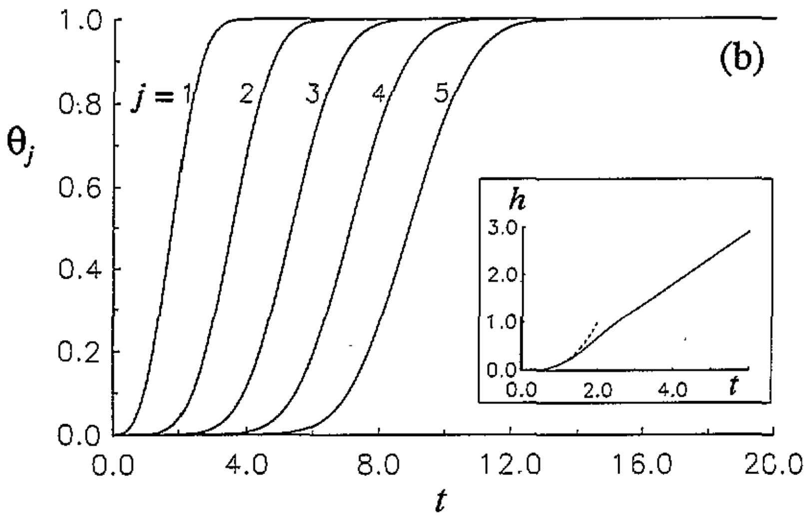


Figure 2. The time dependence of the first five layer coverages (numbered consecutively) in (a) $d=1$ and (b) $d=2$. These were obtained by numerical integration of (5), with the parameter τ set to 2. The time is asymptotically proportional to the film height (see text). The insets show the average film height, in monolayers, as a function of time. The dashed line is the fit of the short-time behaviour, $h \sim (t/\tau)^{d+1}$.

A related quantity of interest, and also directly accessible in film growth experiments, is the instantaneous overall growth rate of the film [20, 28–31, 34], $U(t)=\Sigma_{j\geqslant 1}\,\mathrm{d}\theta_j/\mathrm{d}t$. From (4), it follows that $U(t)$ satisfies

$$U(t)=-\frac{\mathrm{d}}{\mathrm{d}t}\left\{\exp\left[-\left(\frac{t}{\tau}\right)^{d+1}\right]\right\}-\int_0^t \mathrm{d}t'\,U(t')\,\frac{\mathrm{d}}{\mathrm{d}(t-t')}\exp\left[-\left(\frac{t-t'}{\tau}\right)^{d+1}\right] \tag{8}$$

thus its Laplace transform, $u(s)=\int_0^\infty \exp(-st)\,U(t)\,\mathrm{d}t=\mathscr{L}\{U(t)\}$, is

$$u(s)=\frac{1-sf_d(s)}{sf_d(s)} \tag{9}$$

where

$$f_d(s)=\mathscr{L}\left\{\exp\left[-\left(\frac{t}{\tau}\right)^{d+1}\right]\right\}=\sum_{n=0}^{\infty}\frac{(-1)^n s^n \tau^{n+1}}{(d+1)n!}\Gamma\left[\frac{n+1}{d+1}\right]. \tag{10}$$

By Tauberian theorem, $U(t\to\infty)=U_\infty=\lim_{s\to 0} su(s)=(d+1)/\{\tau\Gamma[1/(d+1)]\}$, with $\Gamma[\ ]$ the Gamma function. This agrees with and confirms the heuristic, but more direct analysis above. In figure 3 we plotted layer and total growth rates, and compared the latter with exact asymptotic values.

The film interface width, $w(t)$ is related to the variance of N_j by [35]

$$w^2(t)=\sum_{j=1}^{\infty}(j-h)^2N_j(t)=\sum_{j=0}^{\infty}(2j+1)\theta_j(t)-\left[\sum_{j=0}^{\infty}\theta_j(t)\right]^2. \tag{11}$$

This quantity is shown in figure 4 using the first five layer coverages in the calculation, in one and two dimensions. Note the persistence of oscillations in $d=2$, as compared to the one-dimensional case, an indication that the film is rougher in the latter. Also, at all but small film heights, the range of width values is almost 50% larger in one dimension than in two. The average 'final' slope in corresponding $\log(w)$ versus $\log(t)$ plots give $\beta=(d=1)\simeq 0.33\pm 0.03$ and suggest $\beta(d=2)\simeq 0.27\pm 0.03$. In spite of the small number of layers considered, the former value is in excellent agreement with the exact [18] KPZ $\beta(d=1)=\frac{1}{3}$-value, and the latter is consistent with all recent numerical estimates [36] of $\beta(d=2)$, although centred higher than the previously conjectured [37] $\beta(d=2)=\frac{1}{4}$.

For finite times and infinite substrates, the N_j-distribution is not necessarily Gaussian and can yield non-zero skewness of the interface fluctuations. The skewness is defined by the ratio [38]

$$S(t)=\frac{\sum_{j=1}^{\infty}(j-h)^3N_j}{[w^2(t)]^{3/2}}. \tag{12}$$

Krug *et al* [38] estimated $|S|\approx 0.29$, for one-dimensional KPZ models in the asymptotic regime. This value is expected to be universal [38, 39], its sign given by the sign of the coefficient of the nonlinearity in the KPZ equation (which as argued in the introduction is positive for the PNG model). Our data is shown in figure 5. In spite of strong initial oscillations, they clearly point ot a non-zero positive asymptotic value for S, both in $d=1$ and 2, around 0.3 in the former, and at least an order of magnitude smaller in the latter.

Assuming equivalent scattering factors from substrate and film monolayers, the scattered amplitude at the anti-Bragg condition is simply [40, 41]

$$A(t)=\sum_{j=1}^{\infty}(-1)^{j+1}N_j(t)=\theta_0(t)-2\theta_1(t)+2\theta_2(t)-\dots \tag{13}$$

so the out-of-phase Bragg intensity is $I_{\mathrm{Br}}=A^2$, normalized to unity for a clean substrate. Oscillations in I_{Br}, roughly with the period of monolayer completion, are usually present at the early stages of film growth. They will persist indefinitely for near layer-by-layer steady-state growth, but their amplitude decays for a growth process where the film interface roughens. This is the case here, as shown in figure 6. Note that the minima in the Bragg oscillations do not occur exactly at half-integer monolayers, consistent with the fact that growth on each layer starts before the previous layer is completed. This is a common picture in realistic film growth models.

One of the most interesting features of the Kaschchiev model is its analytic 'solution' in *any* dimension, with non-trivial scaling behaviour. Potential exact analysis of its

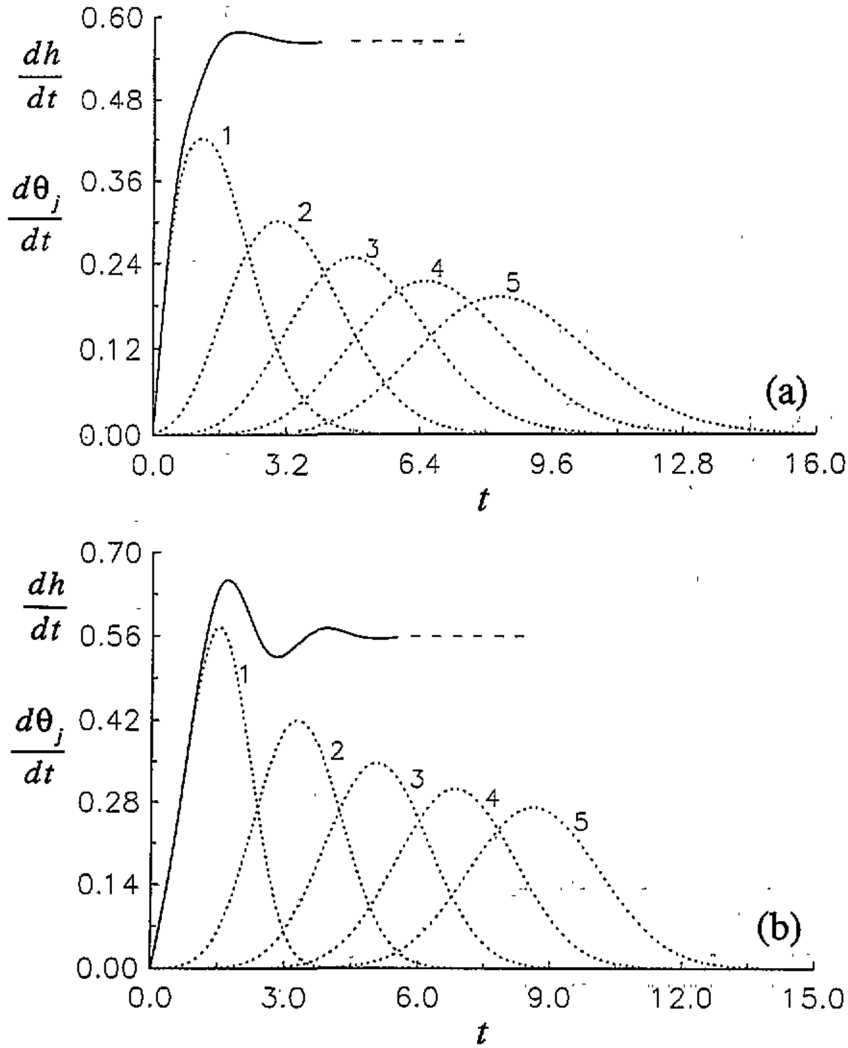


Figure 3. The total growth rate, dh/dt (solid curve), and the individual layer growth rates, $d\theta_j/dt$ (tiny-dashed curves, numbered consecutively according to the layer index), in (*a*) $d=1$ and (*b*) $d=2$, as functions of time, with $\tau=2$. The dashed horizontal segment indicates the exact asymptotic value of the total growth rate, (*a*) $1/\Gamma[\frac{1}{2}]=1/\sqrt{\pi}=0.564\,1896\ldots$, and (*b*) $3/(2\Gamma[\frac{1}{3}])=0.559\,923\ldots$.

asymptotics in $d\geqslant 2$, a formidable challenge in all reported models, would resolve several current questions, like the existence of an upper critical dimension (above which noise fluctuations are irrelevant and $\beta=0$), and the exact value of $\beta(d\geqslant 2)$. This is currently under investigation.

5. Spatial correlations for the growing surface

The behaviour of spatial correlations in these multilayer models is also of interest. For the monolayer Kolmogoroff–Avrami model [12, 13], the two-point correlation functions

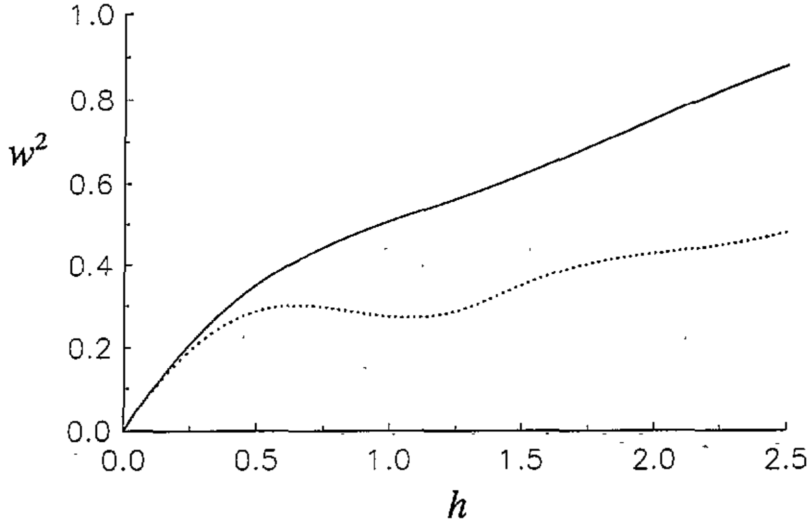


Figure 4. The square of the interface width, w^2, as a function of the total coverage, h, in monolayers. The solid line corresponds to $d=1$ and the dashed line to $d=2$. The 'final' slopes in corresponding $\log(w)$ versus $\log(t)$ plots suggest exponent estimates, $\beta(d=1) \approx 0.33 \pm 0.03$, and $\beta(d=2) \approx 0.27 \pm 0.03$.

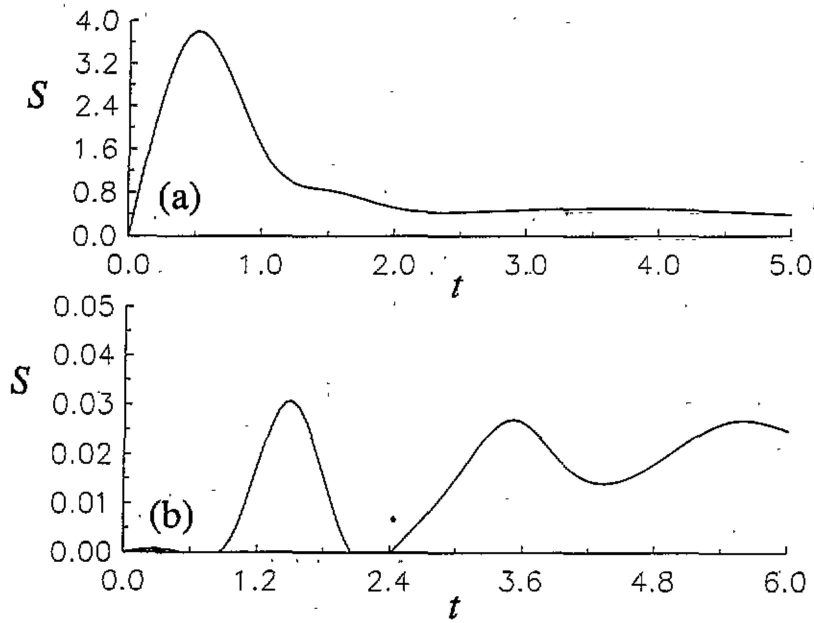


Figure 5. Time dependence of the skewness of the distribution of exposed steps in (a) $d=1$ and (b) $d=2$, with $\tau=2$.

are known exactly [23, 42], for general growth parameters and dimensionality. For two points in the first layer separated by a lateral vector $\boldsymbol{r}$, the probability that both are *uncovered* at times t_1 and t_2, respectively, involves the $(d+1)$-dimensional volume (the extra dimension corresponding to time) of the union of two growing islands nucleated at points separated by $\boldsymbol{r}$ at times t_1 and t_2. For general d and island shapes, the explicit evaluation of this volume is cumbersome. Expressions for 'spherical' islands

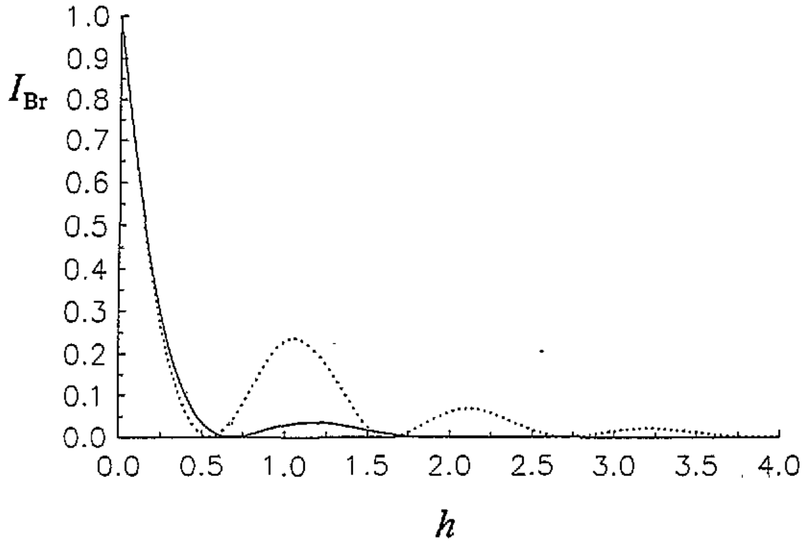


Figure 6. Normalized anti-Bragg intensity as a function of total coverage, h, in monolayers. The solid line corresponds to $d=1$ and the dashed line to $d=2$.

in $d=1-3$ can be found in [23]. The monolayer n-point correlations will involve the n-island volume defined similarly. When $\boldsymbol{r}=0$ the 'two' islands overlap. When $|\boldsymbol{r}| \geqslant (2t'-t_1-t_2)v_1$, for some time $t'>t_1, t_2$, the union of volumes is simply their sum and the joint probability factors into single-point functions, as expected. Thus for finite spreading speeds of the islands, the correlations are strictly finite-ranged, at all finite times. The same is true in higher layers.

The extension to multilayer two-point correlations can be done in a few more steps. Let's start with $\theta_{i|j}(\boldsymbol{r}, t_1|t_2)$, the probability that a point in layer $i \geqslant 1$ is covered with an island at time t_1, *given* that a point in layer $1 \leqslant j \leqslant i$ separated laterally by $\boldsymbol{r}$ is covered with an island at time t_2. The probability conditioning is redundant or trivial when $t_1<t_2$ and $|\boldsymbol{r}| \leqslant (t_2-t_1)v_i$, since that point in layer j is automatically covered due to expansion of the island that covers the point in layer i, or some other island. We develop recursion relations for such quantities, using a simple extension of the arguments that led to (4). Suppose an infinitesimal increment $\mathrm{d}\theta_{i|j}(\boldsymbol{r}, t_1'|t_2)$ is produced due to the creation of an infinitesimal platform around the point in layer i at time t_1'. The fraction of this platform covered by layer $i+1$ at time $t_1>t_1'$ (*given* that a point in layer $1 \leqslant j \leqslant i$ separated laterally by $\boldsymbol{r}$ is covered with an island at time t_2) is the same fraction of the substrate covered in the submonolayer problem at time t_1-t_1', at the rates appropriate for layer $i+1$, i.e. the conditioning does not change the fraction filled. Thus one obtains

$$\frac{\mathrm{d}\theta_{i+1|j}(\boldsymbol{r}, t_1|t_2)}{\mathrm{d}\theta_{i|j}(\boldsymbol{r}, t_1'|t_2)} = 1-\exp\left[-\left(\frac{t_1-t_1'}{\tau_{i+1}}\right)^{d+1}\right] \qquad i \geqslant j. \tag{14}$$

In integral form one has

$$\theta_{i+1|j}(\boldsymbol{r}, t_1|t_2) = \int_0^{t_1} \mathrm{d}t_1' \left[1-\exp\left(\frac{t_1-t_1'}{\tau_{i+1}}\right)^{d+1}\right] \frac{\mathrm{d}}{\mathrm{d}t_1'}\, \theta_{i|j}(\boldsymbol{r}, t_1'|t_2) \qquad i \geqslant j. \tag{15}$$

Using (15), one can construct all $\theta_{i|j}$ with $i>j$ starting from $\theta_{1|1}$ whose expression is known given the joint probabilities derived by Ohta *et al* [23] and Sekimoto [42]. Relation (15) trivially recovers (4) if j is set to zero.

Lastly, one needs to determine all $\theta_{i|i}$ when $i>1$ which involve the quantities $\theta_{i|i+1}=\theta_{i+1|i}(\theta_i/\theta_{i+1})$, determined from the above. As before, let $d\theta_{i|i+1}(\boldsymbol{r}, t_1'|t_2)$ be an infinitesimal increment in the conditional probability $\theta_{i|i+1}$, due to the creation of an infinitesimal portion in layer i. If $t_2 \geq t_1'$, the fraction of this infinitesimal platform covered at time $t_1>t_1'$ is given by the function $\theta_{1|1}(\boldsymbol{r}, t_1-t_1'|t_2-t_1')$, the two-point conditional probability function in the submonolayer problem (evaluated with nucleation and expansion rates characteristic of layer $i+1$). Thus, for $t_2 \geq t_1'$, one obtains

$$\frac{d\theta_{i+1|i+1}(\boldsymbol{r}, t_1|t_2)}{d\theta_{i|i+1}(\boldsymbol{r}, t_1'|t_2)}=\theta_{1|1}(\boldsymbol{r}, t_1-t_1'|t_2-t_1'). \tag{16}$$

This yields the complete solution if $t_2 \geq t_1$ via $\theta_{i+1|i+1}=\int_0^{t_1} dt_1'\, \theta_{1|1}\, d/dt_1'(\theta_{i|i+1})$. The conditioning is trivial, if $|\boldsymbol{r}| \leq (t_2-t_1)v_{i+1}$, and the latter equation reduces to (4), noting that then $\theta_{1|1} \to \theta_1$, $\theta_{i+1|i+1} \to \theta_{i+1}$ and $\theta_{i|i+1} \to \theta_i$. The case where $t_2<t_1$ is more complicated, since one must also consider the regime $t_2<t_1'<t_1$ where $d\theta_{i+1|i+1}/d\theta_{i|i+1}=\theta^*_{1|1}$, say, and $\theta^*_{1|1}$ equals the probability that a point at the origin is filled at time t_1' given that an island of radius $(t_1'-t_2)v_{i+1}$ was nucleated at $\boldsymbol{r}$ at time t_2. Thus $\theta^*_{1|1}=\theta_{1|1}(\boldsymbol{r}^*, t_1-t_1'|0)$, $\boldsymbol{r}^*$ being the closest point to the origin at t_1' of an island nucleated at $\boldsymbol{r}$ at t_2. Here we use the equality of conditional probabilities that the origin is filled given a region is filled, and that the origin is filled given the closest point to the origin in that region is filled. Finally, $\theta_{i+1|i+1}=\int_0^{t_2} dt_1'\, \theta_{1|1}\, d/dt_1'(\theta_{i|i+1})+\int_{t_2}^{t_1} dt_1'\, \theta^*_{1|1}\, d/dt_1'(\theta_{i|i+1})$. This relation correctly recovers $\theta_{i+1|i+1}=1$ if $|\boldsymbol{r}| \leq (t_1-t_2)v_{i+1}$, noting that then $\theta_{1|1}=\theta^*_{1|1}=1$ and $\theta_{i|i+1}=1$.

Finally we comment on the analysis of height-height correlations. One starts with the pair probabilities $\theta_{ij}(\boldsymbol{r}, t)[=\theta_{i|j}(\boldsymbol{r}, t|t)\theta_j(t)]$ for sites in layers i and j, separated laterally by $\boldsymbol{r}$, to be covered at time t. From these one can construct (using simple probability conservation) the height-height probabilities $h_{ij}(\boldsymbol{r}, t)=\theta_{ij}(\boldsymbol{r}, t)-\theta_{i+1j}(\boldsymbol{r}, t)-\theta_{ij+1}(\boldsymbol{r}, t)+\theta_{i+1j+1}(\boldsymbol{r}, t)$ for these sites *not* to be covered by higher layers at time t. One would then analyse the behaviour of the height correlation function [1–4] $G(\boldsymbol{r}, t) \propto \sum_{ij} (i-j)^2 h_{ij}(\boldsymbol{r}, t) \sim |\boldsymbol{r}|^{2\alpha}$, for large t. In principle this could be done analytically (for moderate t), but in practice simulations would be more efficient.

6. Conclusions

In summary, we presented a detailed analysis of the initial evolution of a model of nucleation-controlled multilayer growth. Layer coverages and related measures of film growth and roughness were obtained by numerical integration of Kashchiev's recursion relations. Our results confirm scaling postulated for these models: they behave asymptotically (after 4–5 complete layers) as the KPZ model. We extended the work done for the two-point occupancy probabilities in the submonolayer Kolmogoroff–Avrami model to the multilayer case. Inter and intralayer probabilities are fully determined given the submonolayer results.

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References

[1] Godrèche C (ed) 1991 *Solids Far From Equilibrium: Growth, Morphology and Defects* (Cambridge: Cambridge University Press)

[2] Family F and Vicsek T (ed) 1991 *Dynamics of Fractal Surfaces* (Singapore: World Scientific)

[3] Vicsek T 1989 *Fractal Growth Phenomena* (Singapore: World Scientific)

[4] Family F 1990 *Physica* **168A** 561 and references therein

[5] Villain J 1991 *J. Physique* **I1** 19

[6] Lai Z-W and Das Sarma S 1991 *Phys. Rev. Lett.* **66** 2348

[7] Kang H C and Evans J W 1992 *Surface Sci.* **271** 321

[8] Meakin P and Krug J 1992 *Phys. Rev.* A **46** 3390

[9] Larson P K and Dobson P J (ed) 1988 *Reflection High-Energy Electron Diffraction and Reflection Imaging of Surfaces* (New York: Plenum)

[10] Vetter K 1967 *Electrokhimicheskaya Kinetika* (Moscow: Khimiya)

[11] Kashchiev D 1977 *J. Cryst. Growth* **40** 29

[12] Kolmogoroff A N 1937 *Bull. Acad. Sci.* URSS (Cl. Sci. Math. Nat.) **3** 355

[13] Avrami M 1939 *J. Chem. Phys.* **7** 1103; 1940 **8** 212; 1941 **9** 177

[14] Johnson W A and Mehl P A 1939 *Trans. A.I.M.E.* **135** 365

[15] Sanders D E and Evans J W 1988 *Phys. Rev.* A **38** 4186

[16] Evans J W, Burgess D R and Hoffman D K 1983 *J. Chem. Phys.* **79** 5011

[17] Amar J and Family F 1990 *Phys. Rev. Lett.* **64** 543

[18] Kardar M, Parisi G and Zhang Y-C 1986 *Phys. Rev. Lett.* **56** 889

[19] Goldenfeld N 1984 *J. Phys. A: Math. Gen.* **17** 2807

[20] Armstrong R D and Harrison J A 1969 *J. Electrochem. Soc.* **116** 328

[21] Yamada Y, Hamaya N, Axe J D and Shapiro S M 1984 *Phys. Rev. Lett.* **53** 1665

[22] Axe J D and Yamada Y 1986 *Phys. Rev.* B **34** 1599

[23] Ohta S, Ohta T and Kawasaki K 1987 *Physica* **140A** 478

[24] Sekimoto S 1984 *Physica* **125A** 261

[25] Ishibashi Y and Takagi Y 1971 *J. Phys. Soc. Japan* **31** 506

[26] Venables J A, Spiller G D J and Handbücken M 1984 *Rep. Prog. Phys.* **47** 399

[27] Allen S M and Cahn J W 1979 *Acta Metall.* **27** 1085

[28] Rangarajan S K 1973 *J. Electroanalyt. Chem. and Interfacial Electrochem.* **46** 125

[29] Oldfield J W 1973 *Electodeposition and Surface Treatment* **2** 395

[30] Frank F C 1974 *J. Cryst. Growth* **22** 233

[31] Gilmer G H 1980 *J. Cryst. Growth* **49** 465

[32] Krug J and Spohn H 1989 *Europhys. Lett.* **8** 219

[33] Bennett C H, Büttiker M, Landauer R and Thomas H 1981 *J. Stat. Phys.* **24** 419

[34] Weeks J D and Gilmer G H 1979 *Adv. Chem. Phys.* **40** 157

[35] Thomsen M and Madhukar A 1987 *J. Cryst. Growth* **80** 275

[36] Tang L-H, Forrest B M and Wolf D E 1992 *Phys. Rev.* A **45** 7162

[37] Kim J M and Kosterlitz J M 1989 *Phys. Rev. Lett.* **62** 2289

[38] Krug J, Meakin P and Halpin-Healy T 1992 *Phys. Rev.* A **45** 638

[39] Amar J G and Family F 1992 *Phys. Rev.* A **45** R3373, 5378

[40] van Hove J M, Lent C S, Pukite P R and Cohen P I 1983 *J. Vac. Sci. Technol.* **B1** 741

[41] Lent C S and Cohen P I 1985 *Surface Sci.* **139** 121

[42] Sekimoto K 1984 *J. Phys. Soc. Japan* **53** 2425; 1984 *Physics Lett.* **105A** 390