Kinetic Monte Carlo Simulation of Epitaxial Thin Film Growth: Formation of Submonolayer Islands and Multilayer Mounds

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Keywords
Chemistry, Physics & Astronomy, epitaxial growth, metallic epitaxial layers, monolayers, multilayers, Monte Carlo methods, silver

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Comments
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Kinetic Monte Carlo Simulation of Epitaxial Thin Film Growth: Formation of Submonolayer Islands and Multilayer Mounds

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Abstract. We consider homoepitaxy (or low-misfit heteroepitaxy) via vapor deposition or MBE under UHV conditions. Thin film growth is initiated by nucleation and growth of 2D islands in the submonolayer regime. For atoms subsequently deposited on top of islands, a step edge barrier often inhibits downward transport and produces kinetic roughening during multilayer growth. Such unstable growth is characterized by the formation of 3D mounds (multilayer stacks of 2D islands). Kinetic Monte Carlo (KMC) simulation of suitable atomistic lattice-gas models can address fundamental or general issues related to both submonolayer and multilayer film evolution, and can also provide a predictive tool for morphological evolution in specific systems. Examples of the successes of KMC modeling are provided for metal homoepitaxial film growth, specifically for contrasting behavior in the classic Ag/Ag(100) and Ag/Ag(111) systems.

Keywords: homoepitaxial growth, islands, mounds, lattice-gas models, KMC simulation
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INTRODUCTION

For homoepitaxial growth by vapor deposition or molecular beam epitaxy (MBE) on single-crystal surfaces under ultra-high-vacuum (UHV) conditions, the basic components are as follows \cite{1, 2}: atoms are deposited at random on a periodic array of adsorption sites at rate $F$ per site (the deposition flux); these atoms diffuse across the surface leading to the nucleation and growth of 2D islands \cite{3, 4} (or they can attach to preexisting steps on imperfect or vicinal surfaces); subsequently atoms are deposited on top of these islands and either diffuse to their edges and descend (often with some inhibition due to the presence of an Ehrlich-Schwoebel step-edge barrier to downward transport \cite{5, 6}) or nucleate new islands in higher layers. See Fig.1. A step-edge
barrier thus induces the formation of stacks of 2D islands which are commonly referred to as “mounds” [7]. In the early stages of multilayer growth, the mound sides have small slopes. However, these steepen during growth and often slope selection is ultimately found to occur. In some cases, significant coarsening of the mounds (decreasing their density and increasing their lateral size) also occurs during late-stage growth [1,2].

![FIGURE 1](image-url)  
**FIGURE 1.** Schematic of the key processes underlying homoepitaxial thin film growth for a fcc(100) crystal geometry. Key parameters are: $F =$ deposition flux, $T =$ surface temperature, $E_d =$ terrace diffusion barrier, $E_{Sch} =$ step edge barrier, $E_{bond} =$ NN bond strength. (Copyright Plenum Press, 1997)

Early studies of film growth for heteroepitaxial systems exploited TEM and SEM to access island distributions [8]. Mean-field rate equations were developed to describe average island densities and size distributions (at least approximately) [3,9]. For epitaxial thin films, surface-sensitive diffraction techniques were applied to provide at least partial information on kinetic roughening during multilayer growth [10]. Heuristic multilayer rate equations [11], one-dimensional Markovian models [12], and other models [2, 10] were developed to interpret data. However, in the last two decades, scanning tunneling microscopy (STM) has been exploited to provide far more comprehensive information into the morphologies of growing films for both homo- and heteroepitaxial systems [13]. Even for homoepitaxial films where the equilibrium structure is simple (i.e., flat surfaces), deposition drives the system out of equilibrium producing a rich variety of far-from-equilibrium island and mound morphologies [1, 2]. These STM studies coupled with Kinetic Monte Carlo (KMC) simulation of suitable atomistic lattice-gas models have provided extensive insight into fundamental aspects of film growth (e.g., island size distributions, island shapes, and mound structure and evolution). However, the most realistic and successful KMC modeling has also provided a predictive tool for specific systems. In addition, comparison of model predictions with experimental estimates, e.g., of island density,
film roughness, etc., allows extraction of key activation energy barriers (where these can be treated as free parameters in the modeling).

In this article, we illustrate the successes of KMC studies with applications to the homoepitaxial growth of Ag on Ag(100) and on Ag(111) [2]. Discussion of these two classic growth systems has substantial pedagogical value due to their contrasting behavior. Ag/Ag(100) has been regarded (somewhat inappropriately) as the prototype for smooth quasi-layer-by-layer growth [14] due to a small step-edge barrier. In fact, there is some kinetic roughening; mounds are built upon bases of several submonolayer islands and exhibit a complex coarsening dynamics during late stage growth. Ag/Ag(111) has been regarded as the prototype for rough Poisson growth (rapid kinetic roughening) exhibiting wedding-cake-like mound formation due to a large step-edge barrier [15-17]. Each mound is built upon a base of a single island and exhibits little coarsening (but prolonged steepening). The former system has simple near-square island structure and is thus an ideal candidate for tailored computationally efficient modeling which can best address fundamental issues of island distributions and long-time mound coarsening dynamics. The latter system is characterized by complex island and mound shapes, so modeling must incorporate detailed system-specific information and is thus computationally more expensive.

MODEL COMPONENTS AND MODELING STRATEGIES

In addition to the basic features of deposition, adatom diffusion and aggregation into 2D islands within in each layer, and some degree of interlayer transport, complete specification of the film growth model requires prescription of the following [1, 2]:

(i) Deposition dynamics. For submonolayer growth, atoms are added almost randomly at fcc three-fold hollow [four-fold hollow] adsorption sites on fcc(111) [fcc(100)] surfaces. However, for multilayer growth, one must account for the “downward funneling” to adsorption sites in lower layers of atoms deposited right at step edges and on the sides of nano-protrusions [18]. For fcc(100) systems, this non-activated downward transport process produces unexpected smooth growth at low surface temperatures (T) and can play a key role in mound slope selection at higher T.

(ii) Dynamics of sub-stable clusters of adatoms within each layer. In traditional modeling, a critical size of i (atoms) is prescribed above which islands are stable, i.e. stable clusters are typically formed by aggregation of one additional diffusing adatom with a critical cluster. Then, a key parameter is the binding energy, E<0, of critical clusters as this controls their population and thus the nucleation rate for stable islands [3]. In more fundamental modeling, one instead appropriately specifies the (attractive) interactions between adatoms, so there is no prescribed critical size [19].

(iii) Periphery diffusion (PD) of adatoms along island edges. The efficiency of PD controls the extent of island shape relaxation and compactification during deposition. Limited PD results in dendritic or fractal islands due to the Mullins-Sekerka or DLA instability associated with diffusion-mediated growth [13]. Note that there are numerous local configurations and barriers for atoms diffusing along step edges.

(iv) Interlayer transport. As noted above, downward interlayer transport is often inhibited by a step-edge barrier [5, 6], and this is the critical factor in determining
multilayer mound formation [7]. Thus, one must specify not only the magnitude of this barrier, but also any dependence on local step structure or orientation.

In atomistic modeling, the default choice is that various adatom diffusion processes occur via hopping between adjacent sites. In fact, cooperative exchange processes can in some cases dominate transport either for terrace, step edge, or interlayer diffusion. However, film morphology is determined by the rate or barrier of the diffusion process rather than by the details of the mechanism (which are thus of secondary importance).

While the focus of this article is on KMC simulation of atomistic models, it is appropriate to review simpler approximate treatments for which the KMC results sometimes provide fundamental corrections or improvements. It is also appropriate to note the computational limitations of KMC, particularly for higher T where island formation is highly reversible and there is a higher density of rapidly diffusing adatoms on the surface. Here, there has been considerable interest in integrating KMC into more efficient hybrid treatments, or in developing efficient coarse-grained or continuum formulations which can potentially distill more clearly the essential features of the growth process. Thus, below we first describe these various formulations or treatments of island formation during submonolayer growth, and then present a corresponding description for the multilayer regime. See also Fig. 2 below.

**Treatments of Island Formation during Submonolayer Deposition**

*Mean-Field (MF) Rate Equation Formulations*

In the traditional MF rate equation formulation, one considers a coupled pair of equations for the average densities of adatoms ($N_i$) and islands ($N_{isl}$). Below, densities are measures per site, $h$ denotes the hop rate for terrace diffusion, and $\theta=Ft$ gives the coverage after deposition with flux $F$ for time $t$. These equations have the form [1-4]

$$
\frac{d}{dt}N_i = F(1-\theta) - \sigma_{isl} h N_i N_{isl} - \ldots, \quad \frac{d}{dt}N_{isl} = \sigma_i h N_i N_i,$$

where we retain only the most significant deposition and aggregation terms in the first equation. Also $\sigma_{isl}$ ($\sigma_i$) denotes the capture number for stable islands (critical clusters), and $N_i = c_i \exp[-E_i/(k_B T)](N_i)^\chi$ according to Walton’s relation for the quasi-equilibrated density of critical clusters. Analysis of these equations reveals a short transient regime where $N_i$ increases due to deposition, followed by a steady-state regime where there is a rough balance between gain due to deposition and loss due to aggregation. Balancing these terms in the first equation gives an expression for $N_i$ in terms of $N_{isl}$ which when substituted into the second equation allows simple determination of $N_{isl}$. Thus, one obtains the central result of this analytic MF “nucleation theory” [1-4]

$$
N_{isl} \sim \exp[-E_i/((i+3)(k_B T))] (h/F)^\chi \text{ at fixed } \theta, \text{ with scaling exponent } \chi=(i)/(i+2). \quad (2)
$$

A natural extension of the above formulation considers the densities, $N_s$, of islands of different sizes $s$, where $N_{isl} = \sum_{s=1} N_s$, thus generating the full island size distribution. In developing the appropriate coupled set of rate equations, a key generic term is the
rate of aggregation of diffusing atoms with islands of size \( s \) which is written as 
\[
\sigma_s h N_1 N_s \text{[1-4].}
\]
It is clear that predicted behavior will depend on any assumed size-
dependence of the capture numbers \( \sigma_s \). Thus, some care has been taken to estimate 
these quantities in mean-field treatments subject to the assumption that the 
environment of an island is independent of its size. However, island size distributions 
obtained from these equations are often narrower than those obtained from KMC 
simulation or experiment [4, 20]. The reason for this fundamental failure of MF theory 
(as determined from KMC simulation) is that the environment of an island is in fact 
dependent on its size: a natural consequence of the nucleation and growth process is 
that larger islands are further separated from their neighbors [2, 21].

**KMC Simulation of Atomistic Lattice-Gas Models**

The key challenge in atomistic modeling of epitaxial growth is to develop a lattice-
gas model which incorporates all the essential features of the system of interest. A list 
of typical features is provided at the beginning of this section. Then, KMC simulation 
is in principle rather straightforward [22]; one must simply implement these various 
processes in a stochastic fashion with probabilities in proportion to their rates. The 
stochastic algorithm takes advantage of a random number generator to decide which 
process to implement. The great advantage of KMC modeling (in contrast to standard 
MD simulation) is that one can access relevant time and length scales for deposition.

Since there are often many orders of magnitude difference between the slowest rate 
(e.g., for deposition) and the highest rate (e.g., for terrace or edge diffusion), it is 
necessary to implement a Bortz-type algorithm for efficient KMC simulation [22]. Here, one keeps separate lists of particles in different categories (isolated terrace 
atoms, step edge atoms, etc), which hop with very different rates. Then, processes in 
different categories are implemented according to the relevant total rates (the number 
of particles in the list times the associated hop rate, or the total number of sites times \( F \) 
for deposition). One chooses an entry at random from the relevant list for hopping, or 
chooses a site at random for deposition. However, lists must be updated as adatoms 
shift from one category to another so there is considerable “book-keeping” overhead.

Finally, we quantify the computational inefficiency (which was noted above) of 
KMC for higher \( T \) where island formation is highly reversible. To this end, we have 
performed benchmark simulations for a simple “point-island” model [20, 21] where 
islands occupy a single site but carry a label indicating their size. We analyze behavior 
for various critical sizes \( i \) setting \( E_i=0 \) (so stable islands are formed only when \( i+1 \) 
adatoms randomly meet). If \( T_i \) denotes the CPU time to simulate deposition of 0.1 
monolayers (ML) for \( h/F=10^6 \), we find that [23]

\[
T_2/T_1 = 34, T_3/T_2 = 19, T_4/T_3 = 8.0, T_5/T_4 = 5.4, \text{ etc.,}
\]

and that \( T_i \) roughly scales like the time-integrated density of diffusing adatoms (as 
expected). Thus, if a simulation for \( i=1 \) takes 1 min., that for \( i=5 \) takes 19 days !
This provides strong motivation for development of alternative more efficient algorithms.

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Hybrid, Coarse-Grained or Continuum, and Other Formulations

Conventional KMC simulation algorithms have been modified to incorporate “long hops” for isolated adatoms [24] or to make a hybrid algorithm by replacing atomistic simulation of terrace diffusion with solution of discrete diffusion equations [25]. For the former, the challenge is to develop an efficient local search algorithm to determine of that adatom is close to another adatom or an extended step edge [24]. A coarse-grained or 2D continuum approach describes island edges by a continuous curve and solves a continuum Burton-Cabrera-Frank (BCF)-type deposition-diffusion equation for terrace diffusion with the appropriate boundary conditions at island edges. Nucleation of new islands must still be described stochastically. Level-set [26] or phase-field [27] approaches have been implemented to evolve island morphologies as these can readily accommodate topological changes due to island coalescence. However, the level-set approach is somewhat complex implement, and appropriate expressions for non-equilibrium periphery-diffusion fluxes [2] (determining island growth shapes) have yet to be incorporated. The phase-field approach also cannot reliably describe island growth shapes. One other challenge for these continuum and hybrid approaches is the treatment of reversible island formation the absence of a prescribed critical size [28]. Island breakup must be treated stochastically with a rate accounting for the likely recombination of detaching atoms.

An alternative approach called Geometry-Based Simulation (GBS) exploits a geometric characterization of island growth and nucleation [29]. The surface is tessellated into capture zones (CZ) surrounding each island. Island growth rates are proportional to CZ areas, and nucleation of new islands in the steady-state regime occurs along the boundaries between CZ’s. These locations are furthest from islands where the local adatom density and thus the nucleation rate is highest. Detailed prescription of nucleation positions and rates relies on approximate solution of the steady-state BCF-type deposition-diffusion equation. We should also emphasize that in contrast to a common perception, most nucleation occurs in the steady-state regime (at least for smaller i or larger h/F). To date, the only reliable beyond-MF assessments of the shape of island size distributions for i>3 have come from GBS studies [30, 31].

Treatments of Kinetic Roughening during Multilayer Growth

Multilayer Rate Equations & Single-Mound Step Dynamics Formulations

The height profile of multilayer films is determined by the coverages, \( \theta_n \), for different layers \( n = 1, 2, 3... \) where \( n=0 \) denotes the substrate so \( \theta_0=1 \). Then, \( P_n = \theta_n - \theta_{n+1} \) gives a measure of the exposed fraction of layer \( n \), i.e., the fraction of the film of height \( n \). The film roughness, \( W \), measured in units of interlayer spacing, is obtained from the variance of the film height distribution \( W^2 = \Sigma_n (n-<n>)^2 P_n \), where \( <n> = \Sigma_n n P_n \) (=\( \Theta=\dot{F}t \)) denotes the mean film height [1, 2]. For low step density where crystal geometry is not relevant and downward funneling is ignored, one writes [11]

\[
\frac{d}{dt} \theta_n = F(\theta_{n-1} - \theta_n) - F\alpha_{n-1}(\theta_{n-1} - \theta_n) + F\alpha_n(\theta_n - \theta_{n+1}), \text{ for } n\geq1.
\] (4)
Here, $\alpha_n$ denotes the probability that an atom deposited in layer $n+1$ hops down to layer $n$. Thus, the first two terms represent the net gain due to deposition in layer $n$, and the third term represents gain due to deposition in layer $n+1$. In the case of an insurmountable step edge barrier where $\alpha_n=0$, (4) correctly yields a Poisson film height distribution, $P_n = \exp(-\theta) \frac{\theta^n}{n!}$, for which $W=\theta^{1/2}$. For finite step edge barriers, the form of the $\alpha_n$ depends on the details of film morphology, and only heuristic expressions have been utilized to date for general morphologies [11].

However, for specific classes of film morphologies, a more reliable estimate of the $\alpha_n$ is possible. Consider morphologies consisting of arrays of mounds which are treated as identical, and for which the intervening valleys go down to the substrate. Then, $\theta_n$ is related to the area $A_n$ or effective radius $R_n \propto (A_n)^{1/2}$ of the $n^{th}$ layer in each mound. Also treating these mounds as having circular cross sections, one can solve the deposition-diffusion equations for the annular region corresponding to each layer to determine the attachment flux at each step and thus evaluate $d/dt A_n \propto d/dt \theta_n$ [32]. One also needs a prescription for nucleation of new layers at the peak of the mound. This is usually formulated in terms of a critical radius, $R_c$, for the top layer [33].

These approaches when cast in terms of $d/dt R_n$ equations are naturally described as step dynamics formulations [1, 2, 34]. They have been quite successful in elucidating mound shapes. It was recognized that due to the rare nature of nucleation of top layers, a MF treatment is sometimes not sufficient to determine $R_c$ [1, 35, 36]. These approaches have also been refined to incorporate downward funneling at step edges, and thus to provide insight into mound steepening and slope selection [2, 37, 38].

**KMC Simulation of Atomistic Lattice-Gas Models**

The basic formulation for treating submonolayer growth naturally extends to the multilayer regime. If downward funneling deposition dynamics is significant, then one must incorporate the appropriate fcc crystal geometry and step geometries into the modeling and also suitably prescribe the deposition dynamics [18, 39, 40]. For a fcc(111) surface, distinct local geometries for so-called A- and B-type close-packed step edges with orientations differing by 60° already impact submonolayer growth [1, 2]. CPU time scales roughly in proportion to film thickness, so tailored models and efficient algorithms reap benefits for simulation of the growth of thicker films.

**Coarse-Grained 2D and 3D Continuum Formulations**

The approaches described for submonolayer modeling where step edges are replaced by continuum curves naturally extend to multilayer growth (where one retains a discrete description of vertical film structure). Again either level-set or phase-field formulations can be developed [26, 27], but the challenge of a realistic description of island growth shapes remains. Step edge barrier has not yet been incorporated into level-set treatments, but has been considered heuristically in the phase-field approach [27]. In addition, possible failure of mean-field treatments for the nucleation of top-layer islands [35-36] provides a significant obstacle for these approaches.
In full 3D continuum formulations, one coarse-grains over vertical as well as lateral structure to describe film height by a continuous function, \( h = h(x, t) \) of lateral position \( x \). Then, since here all deposited atoms are assumed to stick to the surface, but then diffuse across the surface with current \( J \), the evolution equation has the form \([1, 2]\)

\[
\frac{\partial h}{\partial t} = F - \nabla_x J + \eta,
\]

with zero-mean random noise term \( \eta \).

\( \text{FIGURE 2. Schematic of different modeling strategies: atomistic; 2D and 3D continuum.} \)

Typically, one makes the decomposition, \( J = J_{\text{NEQ}} + J_{\text{EQ}} \) \([1, 2]\). Here, the “equilibrium” Mullins-type flux has the form \( J_{\text{EQ}} \sim \sigma \gamma \nabla^2 h \) where \( \sigma (\gamma) \) denotes surface mobility (stiffness). However, his flux can be negligible on the time scale of film growth due to effectively irreversible attachment at steps (implying \( \sigma \approx 0 \)). The phenomenological non-equilibrium current is written as \( J_{\text{NEQ}} = J_{\text{SLOPE}}(\nabla h) + J_{\text{SB}} + J_{\text{RELAX}} \). The slope-dependent part is usually assumed to have an uphill component due to reflection from descending steps (due in turn to the step-edge barrier) and biased incorporation at ascending steps, and a downhill component due to downward funneling. These components are taken to cancel at the selected slope \([1, 2]\). Also \( J_{\text{SB}} \) accounts for up-down symmetry breaking, and \( J_{\text{RELAX}} \) for local relaxation at mound peaks and valleys. However, rigorous derivation of these terms remains an open challenge \([37, 41]\).

Integration of (5) produces mound formation, steepening of mound sides, slope selection of (if a downhill current is included), and deterministic coarsening (as the noise term becomes irrelevant) \([42, 43]\). There has been considerable analysis of this deterministic dynamics of coarsening. However, our realistic simulations indicate that in the experimentally relevant regime, coarsening may be fluctuation-dominated. Specifically, fluctuations in the formation of new islands at the peaks of mounds are a key factor triggering one mound to engulf or be engulfed by a neighbor \([2, 44]\).
HOMOEPITAXIAL GROWTH OF AG ON AG(100)

First, we describe our tailored model for Ag/Ag(100) homoepitaxy where island formation is effectively irreversible so \( i=1 \) (below about 320 K). The generic features are: random deposition including downward funneling; terrace and interlayer diffusion and irreversible aggregation of adatoms. However, a special feature for metal(100) systems is facile edge diffusion leading to compact near-square islands except for very low T. The barrier for diffusion along close-packed step edges is well below that for terrace diffusion, but also adatoms at the outer edges of islands can efficiently round at least single-atom high kinks to reach doubly-bonded kink sites, thus propagating compact island shapes. Thus, our simplest modeling appropriate for higher T significantly above 200 K immediately moves adatoms which aggregate at island edges to an accessible kink site on either side of the attachment site [45]. We select a site which can be reached without kink rounding first (anticipating the presence of a kink rounding barrier). For two equally favorable kink sites, various reasonable selection rules can be implemented with similar results. If no kink site is accessible, the adatom remains at the attachment site and nucleates a new outer row when another adatom aggregates with that part of the island edge. This PD dynamics leads to near-square individual islands and a reasonable description of growth coalescence shapes formed when growing islands merge. See the schematic Fig.3

![Figure 3](image)

**FIGURE 3.** Schematic for our model of periphery diffusion (PD) in metal(100) homoepitaxy with efficient transport to kink sites: (a) compact near-square growth of individual islands; (b) development of the “neck region” in growth coalescence shapes for two individual islands. \( P_{kr} \) is the probability for kink rounding in more sophisticated modeling accounting for a significant kink rounding barrier.

For multilayer growth, we find that when prescribing a uniform step edge barrier, the model can mimic kinetic roughening behavior at a single T, but not for different T as observed in an extensive set of experiments [44, 45]. Thus, instead, we prescribe a step-edge barrier of zero on kinked or open step edges, and a finite barrier on close-packed steps [44]. This choice is consistent with predictions from semi-empirical energetics of facile downward transport by an exchange process at kinked steps.

The above algorithm, which avoids explicitly treating PD, results in considerable computational savings allowing ready simulation of multilayer growth into the regime of 1000’s layers. However, experiments indicate that for T near 200 K, rounding of
kinks by edge atoms is inhibited leading to development of irregular island shapes (since aggregating adatoms get “trapped” on outer edges and nucleate new outer rows) [44]. Clearly, a full treatment of PD could address this phenomenon, but would be computationally expensive. We have thus developed an approximate algorithm which accounts for inhibited kink rounding, but which still avoids explicit treatment of PD [46]. The basic idea is as follows. When an adatom aggregates with an island at an outer edge where it cannot reach a kink without kink rounding (kr), we calculate the rate, \( R_{kr} \approx 2v \exp(-E_{kr}/(k_BT))/L_e \), at which it would be incorporated at a kink site. This rate depends on the kink rounding barrier, \( E_{kr} \), and on the outer edge length, \( L_e \) (noting that there is a probability of \( 1/L_e \) to be at a site adjacent to the kink). We also estimate the rate, \( R_{agg} \), of aggregation with this outer edge (e.g., assuming uniform attachment at all step sites). Then, \( P_{kr} = R_{kr}/(R_{kr} + R_{agg}) \) gives an estimate of the probability that an adatom aggregating with this outer edge reaches a kink site before being “captured” by another aggregating adatom to nucleate a new row. In our refined modeling, we use this probability to decide whether to move the aggregating adatom to a kink site. If not, it remains at the aggregation site forming the seed for a new row. This model does effectively capture the transition from compact to irregular islands upon lowering T.

FIGURE 4. Submonolayer deposition of Ag/Ag(100): (a) Simulated submonolayer morphologies (light grey) for 0.25 and 0.75 ML at 300 K for \( F=0.055 \) ML/s [45]. (b) Island density \( N_{av} = N_{isl} \) versus temperature for 0.1 ML films deposited with \( F=0.006 \) ML/s [48]. Symbols give experimental STM results. The solid line gives simulation predictions accounting for post-deposition nucleation of islands (as incorporated in the experimental data). The dashed line shows the total density of atoms plus islands exactly when deposition is terminated. (Copyright American Physical Society 2001, 2002).
Submonolayer Deposition: Island Density and Size Distribution

Figure 4(a) shows results from the above simulation model for submonolayer morphologies at 300 K with terrace diffusion parameters matching Ag/Ag(100) \((h= v \exp[-E_d/(k_B T)])\) with \(v=10^{13} \text{s}^{-1}\) and \(E_d=0.40 \text{ eV}\) [45]. Density functional theory (DFT) gives an estimate \(E_d \approx 0.45 \text{ eV}\) [47]. Note that the model describes both shapes of individual compact islands as well as more complex growth coalescence shapes. Average island densities obtained from such simulations at different \(T\) are compared with experimental values in Fig.4(b) confirming the validity of the model [48]. Interpreting the slope of this Arrenhius plot using the basic result (2) with \(i=1\) gives an \(E_d\) estimate consistent with the above value. For lower \(T\) (corresponding to lower \(h/F\)), the simple scaling of (2) breaks down. Furthermore, one must account for the high density of adatoms remaining on the surface when deposition ceases, and the feature

that these can subsequently form additional islands (which are measured in the experimental density). Performing corresponding two-stage simulations to extract \(N_{isl}\) (solid curves) yields good agreement with experiment at lower (as well as higher) \(T\).

Next, in Fig. 5(a), we show some generic results for the island size distribution for varying \(h/F\) from a model for irreversible formation of near-square islands [2]. This distribution is written in the scaled form as \(N_s \approx N_{isl} (s_{av})^{-i} f(s/s_{av})\) where \(s_{av}=0/N_{isl}\) is the average island size, and \(\int dx x^i f(x) = 1\) for \(i=0, 1\) [4, 20]. At 300K, Ag/Ag(100) has \(h/F \approx 10^8\). The mean-field predictions are much narrower and taller as shown in Fig.5(b); limiting MF behavior as \(h/F \rightarrow \infty\) has an “artificial” discontinuous drop to zero [20].

Previous STM studies also explored island formation above 300 K indicating some type of transition at \(\sim 320\ \text{K}\) [2]. Initial modeling assumed that this was a transition to reversible island formation controlled by the nearest-neighbor (NN) ad-dimer bond strength. This lead to an estimate significantly higher than DFT predictions. Plausibly,
this transition instead reflects at least in part the activation of ad-dimer diffusion on the time scale of island formation (a process not included in the above modeling).

**Multilayer Growth: Mound Formation and Evolution**

As noted above, Ag/Ag(100) has been regarded as the prototype for smooth quasi-layer-by-layer growth at 300 K and above [14]. However, while recent experimental studies have confirmed smooth growth at 300 K for the first 20-30 layers, they have also revealed that very rough growth occurs for the next ~1000 layers [2, 44, 49]! Indeed, some degree of kinetic roughening is anticipated since this system is expected to have a finite (but small) step-edge barrier which ultimately leads to the formation of mounds. This morphological development is clear in sequences of STM images of the growing film at 300 K, although mound development is significantly enhanced at lower T. See Fig. 6. However, what is unprecedented is that in this system should actually grow very roughly at 300 K in the regime of thicker films (ultimately becoming rougher at 300 K than at lower T).

![Figure 6: Sequences of STM images (size: 100x100 nm²) for growth of Ag/Ag(100) at 230 K, 260 K, and 300 K with F=0.02 ML/s. Thickness are indicated. Note the development of mounds (bumps).](image)

Next, we describe our successful modeling of multilayer growth for a range of T, which it should be emphasized is a much more demanding challenge than describing behavior at a single T. We have already noted that use of a uniform step-edge barrier fails, and that instead we set the step-edge barrier on kinked or open steps to zero. This leaves the magnitude of the step-edge barrier on close-packed steps as the one remaining free parameter in the model. Its value of $E_{Sch} = 0.07$ eV is chosen to match the experimental W at a single T and single coverage, e.g., $W=1.4$ for $\theta=25$ ML at 230 K [44, 45]. Then, the model has no further free parameters. Does it succeed or fail in
describing complex roughening behavior for a range of $T$? The answer comes from Fig. 7(a) which reveals impressive success in describing $W$ versus $\theta$ simultaneously for 230 K, 260 K, and 300 K. Prediction of $W$ effectively shows success in describing the development of the height of the mounds. Not shown is that the modeling also describes the lateral dimensions of mounds which are built on several submonolayer islands (and thus requires accurate description of island growth coalescence).

How to understand unusual roughening behavior? Three regimes of growth occur (see also Fig. 7(b)): formation of mounds (taking $\sim$30 layers at 300K); steepening of mounds sides; slope stabilization or selection. For higher $T$, the lateral mound size (which scales with submolayer island separation) is larger. Thus, mounds can grow taller before reaching a selected slope and so the film grows rougher. There is some question about the long-time regime of slope stabilization. Theory indicates that the selected slope should be larger [38]. The observed slope could be limited by the finite lateral mound size, and might slowly increase during subsequent mound coarsening.

As noted earlier, continuum theories of mound evolution present a deterministic picture of coarsening [42, 43]. No doubt this picture applies asymptotically for very thick films. However, in the experimentally relevant regime even up to 1000’s of layers, coarsening appears to be a highly complex and cooperative fluctuation-mediated process [44]. See Fig. 8. Previous theoretical analyses focused on estimating fluctuations in the number of atoms deposited on a typical mound (an unusually high value could cause overgrowth of a neighbor), which proved insufficient to drive coarsening [1]. However, currently we are exploring an analysis of fluctuations in the nucleation of top layer islands which does appear to control coarsening [2].

![Figure 7](image_url)

**FIGURE 7.** Kinetic roughening during growth of Ag/Ag(100) with $F=0.02$ ML/s. (a) Roughness, $W$, versus coverage, $\theta$, for growth different $T$. Symbols show STM data and smooth curves show simulation predictions [44]. (Copyright Materials Research Society 2005). (b) Evolution of film roughness, mound diameter, and mound slope for growth at 190 K.
**FIGURE 8.** Simulation results for cooperative fluctuation-mediated coalescence (i.e., coarsening) of mounds during growth of Ag/Ag(100) at 230 K with F=0.02 ML/s [44]. Images are 35×35 nm². The mound in the bottom center of the first image disappears, triggering expansion of its former upper left neighbor. The mound in the upper center is then incorporated by the adjacent lower pair which then coalesce into a single large mound. Fluctuations in the nucleation of top-layer islands appear to control the evolution. (Copyright American Physical Society 2002).

**HOMOEPITAXIAL GROWTH OF AG ON AG(111)**

Since the terrace diffusion barrier of $E_d = 0.10$ eV in this system is very low [1, 2], we focus on film growth in the 100 K - 200 K regime where the characteristic lateral length describing the film morphology is not so large that features of this morphology are influenced by defects (dislocations) in the substrate. Modeling of the Ag/Ag(111) system is significantly more complex than for Ag/Ag(100) primarily because periphery diffusion (PD) is slow (with roughly 3× the barrier for terrace diffusion), leading inhibited island shape relaxation. Consequently, submonolayer islands exhibit transitions between various complex shapes as $T$ is raised from 100 K to 200 K [50]. Somewhat surprisingly, there had been no previous systematic STM study of this regime. The generic features of the model, as for Ag/Ag(100), are: random deposition including downward funneling dynamics; terrace and interlayer diffusion and aggregation of adatoms. For temperatures closer to 100 K, it suffices to assume irreversible island formation. However, in order to accurately describe film growth for higher temperatures, we must incorporate reversibility in island formation, specifically dissociation of ad-dimers, the rate for which is controlled by the NN adatom bond strength. See below. The most complex and system-specific aspects of the modeling pertain to the treatment of PD, so consequently we now describe these in some detail.

Figure 9 provides a schematic of the various edge configurations and hopping processes for a roughly hexagonal island on an fcc(111) surface. Note that consecutive edges have alternating local structure and are designated as A- and B-type steps. A portion of the potential energy surface for edge diffusion around a corner is also shown, where the values of the barriers are indicated for Ag/Ag(111) based on semi-empirical potentials [50]. Note that the binding energy of an adatom to straight A- and B- steps is almost identical as are the step edge energies (resulting in almost perfectly hexagonal equilibrium island shapes). The key features are as follows [50]:

(i) Relaxation of singly-coordinated corner atoms to higher coordinated sites. This process is facile, but also exhibits a strong asymmetry. Relaxation is easier from
corners to A-steps (barrier of ~0.08 eV) than to B-steps (barrier of ~0.15 eV). This feature is termed “corner diffusion anisotropy” [51].

(ii) Slow edge diffusion. The barriers for A- steps (~0.28 eV) and B-steps (~0.31 eV) are somewhat different, but are both roughly 3x the terrace diffusion barrier. 

(iii) Kink and corner rounding. These processes are inhibited by a small additional barrier of ~0.08 eV (~0.05 eV) starting from A-steps (B-steps).

In our modeling, these edge diffusion barriers are adjusted slightly from their semi-empirical values in order to better match experimentally observed island shapes.

For multilayer growth, there has been extensive recent debate regarding the magnitude of the step-edge barrier, which was assumed to be uniform in these previous analyses [52]. Again we find that use of a uniform step-edge barrier cannot reproduce key experimental observations. Thus, we assign different barriers for A- and B-steps (or actually for local portions of the step edge with A- and B- step structure). Semi-empirical studies indicate that the barrier for the A-step is about twice that for the B- step. Thus, we fix this ratio to 2 in our modeling and treat the lower B-step barrier as a free parameter.

**FIGURE 9.** Left frame [50]: schematic of various periphery diffusion (PD) processes for a near hexagonal island on an fcc(111) surface. Alternating edges of a perfect hexagonal island are of A- and B-type as indicated. Large arrows indicate the “corner diffusion anisotropy”. For an atom at the corner, it is easier to reach the A-step than the B-step. Correspondingly for an atom which is singly-coordinated to another atom attached to a straight step edge, it is easier to relax to the B-step than to the A-step. Right frame [50]: Potential Energy Surface (PES) for edge diffusion around a corner, with energies based on semi-empirical potentials for Ag/Ag(111). (Copyright American Physical Society 2005).

**Submonolayer Deposition: Island Shape Transitions**

The island density in this system is very low due primarily to the small terrace diffusion barrier of $E_d = 0.1$ eV. For lower temperatures around 100 K, we observe simple Arrhenius behavior consistent with (2) for $i = 1$. We find that $N_{isl} \approx 0.9 \times 10^{-4}$ (per site) at 100 K. At 130-140 K, there is a transition presumably to reversible island formation [2, 53]. Both our experimental analysis of multilayer growth below, and a
recent DFT estimate indicate that the corresponding magnitude of the NN bond strength of \(~0.18\) eV [54]. This is significantly lower than a previous DFT estimate which suffered from an unusually slow convergence with lateral supercell size.

Figure 10(a)-(c) shows experimental observations for transitions in island shapes from triangular dendrites at \(~120\) K, to isotropic fat fractals at \(~160\) K, to distorted hexagons at \(~200\) K [50]. In addition, Fig.10(d)-(e) shows behavior in “benchmark” model predictions where we have switched off interlayer transport so that the resulting shapes are entirely controlled by the details of PD [50] (but we do not show 2nd layer islands). These shapes are explained within the framework of our model as follows. (a) For the lowest T, only relaxation is operative. Atoms aggregating with island edges often singly-bond to other adatoms or to the end of short chains. Relaxation occurs more efficiently towards B-steps rather than A-steps due to the corner diffusion anisotropy. See Fig.9. Thus, outward growth of fingers occurs more rapidly from the A-steps producing triangular dendrites with envelopes aligned with B-steps [50, 51]. (b) For the highest T, edge diffusion and corner rounding are active leading to compact islands. However, atoms aggregating at the corners are more likely to be steered to A-steps than to B-steps due to the corner diffusion anisotropy. Thus, in the modeling, these steps tend to grow out producing distorted hexagons with longer B-steps [1, 50, 51]. However, in experiment, A-steps tend to be longer for reasons explained below. (c) For intermediate T, edge diffusion and corner rounding are operative but inhibited, so the DLA instability produces fat fractal island shapes.

**FIGURE 10.** Island shape transitions with varying temperature for 0.3 ML deposition of Ag on Ag(111) with \(F=3.5\times10^3\) ML/s [50]. The top row show STM images (300x300 \(\text{nm}^2\)). The bottom row shows simulation predictions (135x135 \(\text{nm}^2\) for D and 200x200 \(\text{nm}^2\) for E,F). Temperatures are: 135 K (A, D); 165 K (B, E); 200 K (C, F). (Copyright American Physical Society 2005).
We now return to the observation that the distorted hexagonal islands at higher T have longer A-steps in experiment (rather than longer B-steps in the benchmark modeling). We attribute this to the effect of interlayer transport with a non-uniform step-edge barrier. Since the barrier at B-steps is lower, most adatoms descend there attaching to B-steps and causing these to grow faster and thus to grow out. Indeed, refined simulations including interlayer transport still produce islands with longer B-steps if one includes a uniform step-edge barrier, but instead produce longer A-steps when the step edge barrier is significantly lower for the B-steps. The multilayer modeling described below uses a barrier for the B-step equal to \( \frac{1}{2} \) that for the A-step.

**Multilayer Growth: Step-Edge Barrier and Mound Morphologies**

As indicated above Ag/Ag(lll) is often regarded as the prototype for rough Poisson-type growth at least below 300 K [15-17, 49]. Indeed, our STM studies of multilayer growth from 100 K- 200 K support this basic picture with \( W \sim c \theta^{1/2} \). See Fig. 11a. The prefactor c at our lowest T \( \sim 120 \) K appears to drop somewhat below unity, presumably due to the higher density of step edges for dendritic islands [50] and thus the more significant role of downward funneling. Note that any modeling with a large step edge barriers and large islands (i.e., low step density), so that downward funneling is negligible, will produce Poisson-type growth as is clear from (4).

![Figure 11](image)

**FIGURE 11.** (a) Evolution of roughness with coverage for growth of Ag/Ag(lll) at 135K and 160K. (b) STM image (125x125 nm\(^2\)) of 3 ML Ag/Ag(lll) film grown at 150K with F = 0.004 ML/s [55].

We now turn to a more detailed consideration of the film growth morphologies, which consist of arrays of wedding-cake like mounds, and to assessment of the step-edge barrier. Figure 11b shows an STM image of the complex landscape obtained for growth of a 3 ML film at 150 K. The lateral cross-sectional shape of the mounds
propagates upward that of the isotropic fat fractal submonolayer islands [50], a feature which highlights the importance of developing a model which can produce the correct submonolayer island shapes before analyzing multilayer growth.

Next, we consider the vertical cross-sectional shape of the mounds, particularly near their peaks. Intuitively, if there was strictly no interlayer transport, then one would expect the mounds to have very pointed peaks: as soon as two atoms land on the top layer terrace no matter how small, a new island is nucleated (for i=1) creating an even smaller top layer terrace. Indeed, this picture is confirmed and quantified by simple step dynamics modeling [34]. However, while the high step-edge barrier precludes any significant interlayer transport for atoms which land on terraces on the side of the mound (as such atoms quickly attach to ascending steps), this is not the case for atoms landing on the top terrace. Those atoms cannot access an ascending step and thus repeatedly interrogate the descending step bordering the top terrace, and most often succeeding in descending [1, 35]. This causes significant growth in size of the top terrace, and in fact the typical size of these top terraces is extremely sensitive to the magnitude of the finite step-edge barrier. This suggests an effective and precise strategy to estimate the size of the step edge barrier: for growth of 3 ML films at 150 K, simulations give an average top layer island size of 2500, 1600, and 1200 atoms for B-step-edge barrier of 0.06, 0.08, 0.10 eV, respectively. This should be compared with the experimental value of 1400 atoms, so the barrier is slightly above 0.08 eV.

Having determined all the model parameters, one can simulate the development of film morphologies for prolonged multilayer growth. In a system like Ag/Ag(111) with a large step-edge barrier, one expects to find little (lateral) coarsening of mounds, but persistent steepening of the mound sides. This feature is illustrated in the simulated growth morphologies shown in Fig. 12 comparing 1 ML and 3 ML films at 150 K.
Finally, it should be noted that a definitive test of the predictive capability of the model comes from elucidating growth morphologies for a range of T, analogous to our prediction of kinetic roughening for a range of T for Ag/Ag(100). Indeed, the lateral cross-sectional shapes of mounds vary dramatically with T deriving from and mimicking the transitions in the submonolayer island shapes [50]. Our modeling naturally incorporates these changes given its success in capturing submonolayer island shapes. Complete success requires also predicting vertical cross-sectional shapes particularly near mound peaks, noting that the top layer terrace size increases dramatically with increasing T. This also requires accurately capturing the degree of reversibility present in island formation, which is only small at 150 K and below, but significant at higher T. Indeed, our modeling is successful in these respects, but only because of a careful accounting of this reversibility. See Ref. [55] for a detailed description of model predictions and comparison with experimental morphologies.

CONCLUSIONS

The above presentation is intended to show the utility of KMC studies of atomistic lattice-gas models for epitaxial film growth. An initial major impact of these studies was the elucidation of submonolayer island formation. In particular, these studies obtained for the first time precise island size distributions [20] and also extracted a detailed understanding of complex island shapes observed in some systems with inhibited PD [1, 2]. In addition, they were effective in elucidating fundamental aspects of mound formation and evolution during multilayer growth, accounting for deviations from mean-field kinetics for top-layer nucleation and for fluctuation effects absent in continuum treatments [1,2]. Finally, we note our considerable success in developing predictive models for Ag/Ag(100) and Ag/Ag(lll) homoeptaxial growth. These models have successfully described (sometimes unexpected) behavior for a broad range of T. In particular, they have captured both complex roughening kinetics for Ag/Ag(100) and intricate features of the film morphology for Ag/Ag(lll).

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