Island nucleation in the presence of step edge barriers: Theory and applications

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We develop a theory of nucleation on top of two-dimensional islands bordered by steps with an additional energy barrier $\Delta E_S$ for descending atoms. The theory is based on the concept of the residence time of an adatom on the island, and yields an expression for the nucleation rate which becomes exact in the limit of strong step edge barriers. This expression differs qualitatively and quantitatively from that obtained using the conventional rate equation approach to nucleation [J. Tersoff et al., Phys. Rev. Lett. 72, 266 (1994)]. We argue that rate equation theory fails because nucleation is dominated by the rare instances when two atoms are present on the island simultaneously. The theory is applied to two distinct problems: The onset of second layer nucleation in submonolayer growth, and the distribution of the sizes of top terraces of multilayer mounds under conditions of strong step edge barriers. Application to homoepitaxial growth on Pt(111) yields the estimate $\Delta E_S \geq 0.33$ eV for the additional energy barrier at CO-decorated steps.

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I. INTRODUCTION

On many metal surfaces an adatom descending across a step edge encounters an additional energy barrier $\Delta E_S$ compared to the diffusion barrier $E_D$ on an atomically flat terrace. This step edge barrier controls the rate of interlayer mass transport and therefore has a decisive influence on the morphology of multilayer films.

A number of papers have addressed the question of how to determine $\Delta E_S$ experimentally. Most approaches start from the observation that the step edge barrier increases the residence time of adatoms on top of an island, and therefore promotes the nucleation of the next layer. Tersoff, Denier van der Gon and Tromp (TDT) presented a quantitative analysis of this effect, which is based on the conventional estimate

$$\omega \sim \nu n^{i^*+1}$$

for the nucleation rate $\omega$ in terms of the in-layer hopping rate $\nu$, the adatom density $n$ and the size $i^*$ of the largest unstable cluster. Equation (1) arises from rate equations for spatially averaged island and adatom densities, and its applicability to the confined geometry on top of an island is not obvious. Other treatments invoke the concept of a critical adatom density for nucleation, which is defined as the density at which nucleation would take place on the unbounded terrace. Again, given the rather different conditions on top of an island, this approach seems hard to justify (see Section III C).

In this paper we present a detailed microscopic analysis of nucleation in the presence of strong step edge barriers, which takes into account the large fluctuations of the adatom population on top of the island. Our expression for the nucleation rate, to be derived in Section II A, differs qualitatively and quantitatively from that obtained by TDT. The rate equation treatment significantly overestimates the nucleation probability, and therefore the analysis of experimental data based on the TDT theory generally gives values for $\Delta E_S$ which are too small. To illustrate our point, we apply our approach to two different experimental situations. In Section II we determine the critical radius for second layer nucleation for submonolayer deposition, and use it to reanalyse the experiments of Bromann et al. for Ag(111), and of Kalff et al. for CO-contaminated Pt(111). In Section III we develop a simple analytic theory for the size of the top terrace of pyramidal multilayer mounds (“wedding cakes”), and apply it to the case of Pt(111). For CO-decorated steps on Pt(111) the two approaches yield mutually consistent estimates for $\Delta E_S$. Some of the results presented in Section III have been independently obtained by Rottler and Maass, who also provide numerical confirmation by Monte Carlo simulations for $i^* = 1$.

II. NUCLEATION RATE ON TOP OF AN ISLAND

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A. Irreversible aggregation with strong barriers

We consider a compact two-dimensional island of area $A$ and perimeter $L$. Both $A$ and $L$ are dimensionless quantities measured in terms of the number of lattice sites on the island ($A$) and the number of edge sites ($L$), respectively. For large $L$ they are related through

$$A = \alpha L^2$$

(2)

where the coefficient $\alpha$ depends on the island shape; for example, $\alpha = 1/16$ for square islands, $\alpha = 1/12$ for regular hexagons on a triangular lattice and $\alpha = 1/4\pi$ for a circular island in a continuum approximation. Atoms are deposited at rate $F$, diffuse on the island (and on the underlying terrace) at rate $\nu = \nu_0 \exp[-E_D/k_B T]$, and descend from edge sites at rate $\nu' = \nu_0' \exp[-E_S/k_B T]$. The additional energy barrier at the step edge is then $\Delta E_S = E_S - E_D$. Since the actual energy landscape on real islands may well be more complicated, $\nu'$ should be regarded as an effective interlayer transport rate.

To arrive at this relation, consider the deposition of noninteracting atoms onto the island during some long time interval $T$. To compute $\Delta t$, suppose the first adatom has arrived on the island at time $t = 0$, and denote by $t_1$ and $t_2$ the departure time of the first adatom and the arrival time of the second one. Since deposition is a Poisson process, $t_2$ is an exponential random variable with mean $\tau$. In the strong barrier limit also the distribution of $t_2$ should be regarded as an exponential distribution.

In this section we further assume that the critical island size takes its minimal value $n = 1$, i.e. the first adatom deposited on the island already forms a nucleus. In this limit the nucleation probability $p_0$ per deposited adatom is equal to the probability $p_2$ that two adatoms are present simultaneously on the island. To compute $p_2$ suppose the first adatom has arrived on the island at time $t = 0$, and denote by $t_1$ and $t_2$ the departure time of the first adatom and the arrival time of the second one. Since deposition is a Poisson process, $t_2$ is an exponential random variable with mean $\tau$. In the strong barrier limit also the distribution of $t_2$ should be regarded as an exponential distribution.

It follows that $\tau/\tau_{tr} \approx \ell_{ES}/L$, and therefore the strong barrier condition is equivalent to $\tau/\tau_{tr} \gg 1$.

In this section we further assume that the critical island size takes its minimal value $n = 1$, i.e. dimers are stable and immobile. Then, as soon as two adatoms are present on the island, nucleation occurs after a time of the order of $t_{tr} \ll \tau$; on the scale of the residence time nucleation is an instantaneous event. We conclude, therefore, that the nucleation probability $p_{nuc}$ per deposited adatom is equal to the probability $p_2$ that two adatoms are present simultaneously on the island. To compute $p_2$, suppose the first adatom has arrived on the island at time $t = 0$, and denote by $t_1$ and $t_2$ the departure time of the first adatom and the arrival time of the second one. Since deposition is a Poisson process, $t_2$ is an exponential random variable with mean $\tau$. In the strong barrier limit also the distribution of $t_2$ should be regarded as an exponential distribution.

Thus $\tilde{n} = FA/L\nu' = \alpha FL/\nu'$ and

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The expression for $p_{\text{nuc}}$ can also be found by using an argument first developed in one dimension by Elkinani and Villain (see Ref. 25 for the two-dimensional case). According to this approach, the nucleation probability per deposited atom is simply the number of distinct sites visited by each adatom (equal to $A$) times the probability that a site is occupied (given by the adatom density $\bar{n}$). Together with (3) this implies $p_{\text{nuc}} = AF\tau = \tau/\Delta t$ as above.

To obtain the nucleation rate $\omega$, defined as the number of nucleation events taking place on the island per unit time, we multiply the nucleation probability $p_{\text{nuc}}$ by the number of atoms arriving on the island per unit time, and obtain, in the relevant case $\Delta t \gg \tau$,

$$\omega = FA \frac{\tau}{\Delta t} = \frac{\alpha^3 F^2 L^5}{\nu'^2}.$$  \hspace{1cm} (9)

This is to be compared to the expression

$$\omega = \frac{\alpha^3 F^2 L^4}{4\nu'^2}$$  \hspace{1cm} (10)

derived from the approach of TDT ($\gamma$ denotes a capture number of order unity). Equation (10) exceeds (9) by a factor $(\nu/\nu')L^{-1} = \ell_{\text{ES}}/L \gg 1$. To explain this discrepancy we note that the mean number of adatoms on the island is much less than unity in the regime of interest. Most of the time the island is empty, and sometimes it is occupied by a single adatom. For example, consider a Pt island on Pt(111) without a second layer nucleus, but at a size, at which about half of the island population has already formed such a nucleus (see Section III E). Even for this island the probability to find an atom on top is only about $10^{-2}$, as is the probability for an atom to become deposited on an island already populated by an atom. For this reason we refer to our approach as the *lonely adatom model* (LAM).

The strong fluctuations in the occupancy of the island imply that the replacement of the actual adatom density by its time average $\bar{n}$, which is inherent in (9), cannot be justified, and must be replaced by the more detailed statistical analysis provided above.

### B. Intermediate and weak barriers

To some extent the considerations of the preceding section can be generalized to the case when the strong barrier condition $\ell_{\text{ES}} \gg L$ is no longer satisfied. The mean residence time is still given by (5), and the mean adatom density $\bar{n}$ can be obtained by solving the stationary diffusion equation with the appropriate boundary conditions. For the case of a circular island of radius $r = L/2\pi$ this yields

$$\tau = \frac{1}{2\nu} \left( r^2 + \frac{\nu r}{\nu'} \right).$$  \hspace{1cm} (11)

However now the probability $p_2$ provides only an upper bound on the nucleation probability $p_{\text{nuc}}$, since one of the two adatoms may escape from the island before the two meet. Also in the evaluation of $p_2$ in eq.(5) the probability distribution $P_{\text{res}}(t_1)$ of residence times has to be used, which is a complicated non-exponential function. The calculation simplifies by noting that for weak barriers surely $\tau \ll \Delta t$; then the exponential distribution of interarrival times can be expanded and one obtains

$$p_2 = \int_0^\infty dt_1 P_{\text{res}}(t_1)(1 - e^{-t_1/\Delta t}) \approx \frac{1}{\Delta t} \int_0^\infty dt_1 t_1 P_{\text{res}}(t_1) = \frac{\tau}{\Delta t}.$$  \hspace{1cm} (12)

We conclude that an upper bound on the nucleation rate for a circular island is given by the expression

$$\omega_\text{> } = \frac{\pi^2 F^2 r^4}{2\nu} \left( r^2 + \frac{\nu r}{\nu'} \right).$$  \hspace{1cm} (13)

If the barriers are weak, $r \gg \ell_{\text{ES}}$, we find $\omega_\text{> } = \pi^2 F^2 r^6/2\nu$, which agrees (up to a numerical prefactor) with Eq. (4a) of TDT. This implies that the rate equation ansatz (9) yields the correct result only when the barriers can be neglected.

### C. Reversible aggregation

We return to the case of strong step edge barriers and analyze reversible aggregation with stable trimers and unstable dimers ($i^* = 2$). The dimer dissociation time $\tau_{\text{dis}}$ introduces a further time scale into the problem. Suppose
that two adatoms are present on the island; this is true with probability $p_2 = \tau/\Delta t$. Let us assume for simplicity that one atom is fixed and the other diffusing. If the two adatoms stay on the island a time $t$, this means that the diffusing atom has failed to descend a number of times of order $j = t/(\tau_{tr} + \tau_{dis})$, which is true with a probability of the order of order $\exp(-j\tau_{tr}/\tau)$. Therefore the effective residence time $\tau'$ of the adatom pair can be estimated as $\tau' \sim \tau(\tau_{tr} + \tau_{dis})/\tau_{tr}$. In the limit $\tau_{tr} \gg \tau_{dis}$, $\tau' \sim \tau$, and in the limit $\tau_{tr} \ll \tau_{dis}$, $\tau' \sim \tau(\tau_{dis}/\tau_{tr})$. The lifetime of the pair is increased compared to the single adatom lifetime if $\tau_{tr} \ll \tau_{dis}$.

Consider first the case $\tau_{dis} \ll \tau_{tr}$, when the total residence time of the two adatoms is still of the order of $\tau$, and a dimer is present a fraction $q \equiv \tau_{dis}/\tau_{tr}$ of that time. The probability for a third atom to deposit while the two atoms are on the island is $\tau/\Delta t$ as before. The third atom traverses the island of the order of $m = \tau/\tau_{tr}$ times, and each time the probability that it encounters a dimer is $q$. We therefore have to distinguish the cases $mq \ll 1$ and $mq \gg 1$.

In the first case the probability that a stable trimer forms is $mq \sim \tau \tau_{dis}/\tau_{tr}$, and altogether the nucleation probability per atom is of the order of

$$p_{nuc} \sim \left(\frac{\tau}{\Delta t}\right)^2 \frac{\tau \tau_{dis}}{\tau_{tr}^2} \sim \frac{F^2 L^3 \nu^2 \tau_{dis}}{\nu^3} \quad \text{for } \tau_{dis} \ll \tau_{tr}^2/\tau \quad \text{(regime I)}. \quad (14)$$

On the other hand, if $mq \gg 1$ the third atom is certain to encounter a dimer, and

$$p_{nuc} \sim \left(\frac{\tau}{\Delta t}\right)^2 \sim \frac{F^2 L^6}{\nu^2} \quad \text{for } \tau_{tr}^2/\tau \ll \tau_{dis} \ll \tau_{tr} \quad \text{(regime II)}. \quad (15)$$

In fact a somewhat more precise statement can be made. In regime II the nucleation probability is equal to the probability $p_3$ of finding three adatoms simultaneously on the island. The calculation in Appendix A shows that, for $\tau \ll \Delta t$, $p_3 = (1/2)(\tau/\Delta t)^2$, and therefore the prefactor in (13) is $\alpha^3/2$.

Next consider the case $\tau_{dis} \gg \tau_{tr}$, when the effective residence time of the first two adatoms is $\tau' \sim \tau(\tau_{dis}/\tau_{tr}) \gg \tau$. If a third atom is deposited onto the island it will find the dimer with a probability close to unity. A third atom will deposit during time $\tau'$ with probability $\tau'/\Delta t$ if $\tau' < \Delta t$ and with probability one if $\tau' > \Delta t$. This implies two further scaling regimes:

$$p_{nuc} \sim \frac{\tau}{\Delta t} \cdot \frac{\tau'}{\Delta t} \sim \frac{F^2 L^4 \nu \tau_{dis}}{\nu^2} \quad \text{for } \tau_{tr} \ll \tau_{dis} \ll \Delta t \cdot (\tau_{tr}/\tau) \quad \text{(regime III)}. \quad (16)$$

$$p_{nuc} \sim \frac{\tau}{\Delta t} \sim \frac{F L^3}{\nu} \quad \text{for } \tau_{dis} \gg \Delta t \cdot (\tau_{tr}/\tau) \quad \text{(regime IV)}. \quad (17)$$

In the last regime the dimer lifetime is so long that the situation effectively reduces to the case $i^* = 1$.

The smallest value that $\tau_{dis}$ can take is the inverse in-layer hopping frequency $1/\nu$. Then $\tau_{dis}/\tau_{tr} \sim L^{-2} \ll 1$ always, but depending on the strength of the step edge barrier both regimes I and II can be realized, corresponding to $L^3 \gg \ell_{ES}$ (regime I) and $L^3 \ll \ell_{ES}$ (regime II), respectively. Setting $\tau_{dis} = 1/\nu$ in regime I (Eq. (14)) yields

$$p_{nuc} \sim \frac{F^2 L^3 \nu}{\nu^3} \quad \text{(regime I, } \tau_{dis} = 1/\nu) \quad (18)$$

which agrees with the expression derived by TDT for $i^* = 2$. This indicates, as suggested by Rottler and Maass,\textsuperscript{[3]} that the rate equation approach describes a situation in which the probability for an encounter between the atoms forming the stable nucleus (the quantity $mq$ in our derivation) is small compared to unity.

The complexity of the case $i^* = 2$ illustrates the difficulty of extending the present analysis to larger values of $i^*$. The generalization seems straightforward only in regime II, where the barriers are sufficiently strong to guarantee the formation of a stable nucleus once $i^* + 1$ atoms are on the island simultaneously (but still so weak that $\tau \ll \Delta t$). Then $p_{nuc} = p_{r+1}$, and using Eq. (12) of the Appendix we obtain

$$p_{nuc} = \frac{1}{i^*!} \left(\frac{\tau}{\Delta t}\right)^{i^*} = \frac{1}{i^*!} \left(\frac{\alpha^2 L^3 F}{\nu'}\right)^{i^*} \quad \text{(regime II, general } i^*). \quad (19)$$

### III. SECOND LAYER NUCLEATION
A. The critical island size

In this section we consider a population of submonolayer islands and ask for the fraction \( f \) of islands on which a second layer has nucleated. Once the nucleation rate \( \omega(L) \) per island is known as a function of island size \( L \), this fraction is given by:

\[
f = 1 - \exp\left[-\int dt \omega(L(t))\right],
\]

where the integration extends over the deposition time, and the functional dependence \( L(t) \) depends on the growth situation. For example, if first layer islands of density \( N \) nucleate at time \( t = 0 \), and no further nucleation occurs at later times, then the island size increases with coverage \( \theta = Ft \) as \( L = \sqrt{\theta/\alpha N} \). Assuming a size dependence of the nucleation rate of the general form

\[
\omega(L) = F\Omega L^k,
\]

where \( \Omega \) is a constant independent of \( L \), one finds

\[
f = 1 - \exp[-(L/L_c)^{k+2}]
\]

where the critical island size \( L_c \) is given by

\[
L_c = \left( \frac{k + 2}{2\alpha N \Omega} \right)^{1/(k+2)}.
\]

In particular, using our expression \( i^* = 1 \) for \( i^* \) we obtain

\[
L_c = \left( \frac{7}{2\alpha^4} \cdot \frac{\nu'}{FN} \right)^{1/7}.
\]

This agrees with the scaling law derived by Rottler and Maass, and specifies the prefactor.

The different regimes for \( i^* = 2 \) discussed in Section II C can be treated in the same way; the results are summarized in Appendix B. Inspection shows that our regime II corresponds to regime II of Rottler and Maass, while our regime I corresponds to their regime III (they assume that the dimers are maximally unstable in the sense that \( \tau_{\text{dis}} = 1/\nu \)).

A critical island size for second layer nucleation can also be defined when the barriers are so strong (or the flux so large) that the condition \( \tau \ll \Delta t \) is no longer fulfilled. Then the nucleation probability per atom becomes of order unity, and the nucleation rate on top of the island is \( \omega \approx FA \). Repeating the above analysis for this case, one finds that

\[
f = 1 - \exp[-\theta^2/2N] = 1 - \exp[-(L/L_\infty)^4]
\]

with \( L_\infty = (2/\alpha^2 N)^{1/4} \). The critical island size is of the order of the square root of the island spacing, independent of \( \nu' \) and \( i^* \). This corresponds to regime I of Rottler and Maass.

B. Conditions for layer-by-layer growth and surfactant action

According to classical nucleation theory, the first layer island density depends on flux and in-layer mobility according to the scaling law

\[
N \sim (F/\nu)^{i^*/(i^*+2)}.
\]

Provided the in-layer mobility on the island is the same as on the terrace, for \( i^* = 1 \) the LAM expression can therefore be written as

\[
L_c \sim \frac{\nu^{1/21} \nu'^{1/7}}{F^{4/21}} \quad \text{(LAM)},
\]

while the corresponding expression of the TDT theory reads
Surprisingly, a decrease of the in-layer mobility $\nu$ is seen to (weakly) decrease the critical island size according to the LAM, but increases it according to the TDT theory.

A decrease of the in-layer mobility is believed to play an important role in the ability of certain adsorbates (such as Sb on Ag(111)) to act as surfactants, in the sense of promoting layer-by-layer growth (Ref. 13). The transition from three-dimensional to layer-by-layer growth occurs when the critical island size becomes comparable to the distance $N^{-1/2}$ between first layer islands. Equating (27) and (28) to $(\nu/F)^{1/6}$ one finds in both cases $L_c \sim \ell_{ES} \sim \nu/\nu'$, which shows that the condition for the onset of layer-by-layer growth does not depend on the details of the second layer nucleation mechanism, at least as long as $\ell_{ES}$ is the only additional length scale in the problem; in the case $i^* = 2$ the dimensionless number $\tau_{dis}\nu$ introduces another scale, and the situation becomes more complicated.

C. Adatom density at second layer nucleation

It was mentioned in Section III that, in addition to the rate equation approach, the problem of second layer nucleation has been treated using the concept of a critical density for nucleation (Ref. 14). To see whether such a concept is meaningful in the present context, we can estimate the mean adatom density $n_c$ on top of a first layer island at the time of second layer nucleation. Using (5) and (7) we obtain

$$n_c \sim \frac{(F/\nu')^{6/7} N^{-1/7}}{L_c^{-6} N^{-1}}.$$  

This is to be compared to the adatom density $n_{sub}$ on the substrate at the time of first layer nucleation, which is of the order $n_{sub} = (F/\nu)N^{-1} \sim N^2$ for $i^* = 1$. The comparison shows that $n_c \gg n_{sub}$ provided $L_c$ is small compared to the mean island spacing, which is equivalent to the condition of strong step edge barriers (see Section III B). Thus in the regime of interest, the assumption $n_c \approx n_{sub}$ is not satisfied, and consequently the estimates of $L_c$ obtained in Refs. 6 and 7 are not quantitatively accurate.

D. Nucleation on predeposited islands: The case of Ag(111)

A detailed experimental study of second layer nucleation on Ag(111) was performed by Bromann et al. (Ref. 8). They prepared arrays of approximately circular islands of uniform initial radius $r_0$ through Ostwald ripening at high temperatures. Given the initial coverage $\theta_0$, the island density is then $N = \theta_0/\pi r_0^2$. Subsequently a second dose of coverage $\Delta \theta$ was deposited, and the fraction $f$ of islands with second layer nuclei was measured as a function of $r_0$. Independent evidence shows that the critical nucleus size is $i^* = 1$ under the experimental growth conditions. Provided further nucleation during the second dose can be neglected, the island radius increases with coverage according to $r = r_0 \sqrt{1 + \theta/\theta_0}$. Inserting this into (4) and using that $\theta_0 = \Delta \theta$ in the experiment, we find

$$f = 1 - \exp[-(r_0/\tilde{r}_c)^5]$$

with

$$\tilde{r}_c = \left(\frac{7}{\pi^2(27/2 - 1)} \cdot \frac{\nu'}{F \Delta \theta}\right)^{1/5}.$$  

The step edge barrier can be extracted directly by comparing the critical radii at two different temperatures $T_1$ and $T_2$, since according to (31)

$$\tilde{r}_c(T_1)/\tilde{r}_c(T_2) = \exp[E_S(T_2^{-1} - T_1^{-1})/5k_B].$$

From Figure 2 of Ref. 8 we estimate that $\tilde{r}_c \approx 28 \text{Å}$ at 120 K and $\tilde{r}_c \approx 52 \text{Å}$ at 130 K. This yields $E_S \approx 0.42 \text{ eV}$, leading to an additional step edge barrier $\Delta E_S \approx 0.32 \text{ eV}$. The theory of TDT predicts instead that $\tilde{r}_c \sim (\nu'^2/\nu)^{1/4}$, which implies

$$\tilde{r}_c(T_1)/\tilde{r}_c(T_2) = \exp[(2E_S - E_D)(T_2^{-1} - T_1^{-1})/4k_B]$$

and yields the estimate $\Delta E_S \approx 0.12 \text{ eV}$ reported by Bromann et al. (Ref. 8).
The dramatic discrepancy between the two estimates for $\Delta E_S$ makes it important to examine also the prefactor $\nu_0'$ in the expression for $\nu'$. Using (31) with $E_S = 0.42$ eV yields $\nu_0' \approx 8 \times 10^{19}$ s$^{-1}$, which seems much too large to be physically reasonable. Smaller values of $\nu_0'$ can be obtained if a (slight) temperature dependence of the barrier is permitted. Since the step edge barrier of interest here in fact constitutes an average over the (temperature-dependent) step structure, such a dependence could be expected due to thermal roughening of the step edge. For example, if we demand that the prefactor be the same as for in-layer transport, $\nu_0 = \nu_0 = 2 \times 10^{11}$ s$^{-1}$, then (31) yields $E_S \approx 0.21$ eV at $T = 120$ K and $E_S \approx 0.20$ eV at $T = 130$ K, somewhat smaller than the estimate $E_S \approx 0.22$ eV of Bromann et al. while taking their value $\nu_0 = 10^{13}$ s$^{-1}$ for the prefactor, yields the larger barrier $E_S = 0.26$ eV ($T = 120$ K) and $E_S = 0.24$ eV ($T = 130$ K), respectively. The effective barrier decreases with increasing temperature, which is consistent with the step roughening picture. Clearly a more definite statement about the values of $E_S$ and $\nu_0'$ on the Ag(111) surface requires a detailed reanalysis of the experimental data, and perhaps also additional measurements.

E. Application to Pt(111) islands with decorated steps

In this section we use the LAM to analyze the dependence of $\nu'$ and $\Delta E_S$ on the CO partial pressure $p_{CO}$ in Pt homoepitaxy on Pt(111). CO exposure during growth leads to step decoration, which impairs the hopping of adatoms over the step edge and therefore increases $\Delta E_S$ (for details see Ref. 13).

Rather than following the evolution of the fraction $f$ of islands with second layer nuclei with coverage or island size, we employed a method which requires only a single growth experiment within the appropriate coverage range, i.e. a growth experiment which creates islands partly with and partly without second layer nuclei. The practical analysis is performed by determination of the number of edge steps $L$ of the largest islands without a second layer island on top and of the smallest islands with a second layer one on top for a statistically significant number of topographs. The averages of the two sets of values vary typically by less than 10%. The mean of the two averages then gives an estimate of the island size $L_{1/2}$ defined by $f(L_{1/2}) = 1/2$: at this island size it is equally likely to find an island with or without a second layer nucleus. Using Eqs. (22,24) for $i^*$ = 1, one obtains the expression

$$\nu' = \frac{2}{7\ln 2} \alpha^4 FNL^2_{1/2}$$

(34)

for $\nu'$ in terms of $L_{1/2}$.

In order to translate $\nu'$ into the additional step edge barrier $\Delta E_S$, it is necessary to make assumptions on the adatom migration energy $E_D$ and the attempt frequency $\nu_0'$ for hopping over the step edge. For the case of Pt adatoms on Pt(111), $E_D$ was found to be 0.26 eV in two independent experimental studies, and the prefactors agreed within a factor of two with an average of $\nu_0 = 8 \times 10^{12}$ s$^{-1}$. An estimate of $\nu_0'$ for the clean case can be obtained from a Field Ion Microscopy study, in which the adatom residence time was directly measured. Using the relation for circular islands, the prefactor obtained in Ref. 19 translates into $\nu_0' \approx 7 \times 10^{11}$ s$^{-1}$, somewhat smaller than $\nu_0$. However, since nothing is known about the effect of CO decoration on $\nu_0'$, in the following we take $\nu_0'$ to be identical to $\nu_0$ for simplicity. The growth experiments were carried out at 400 K with a deposition rate $F = 5 \times 10^{-3}$ ML/s.

The open circles in Fig. 1 exhibit the critical size $L_{1/2}$ as a function of the applied CO partial pressure during growth, as derived from Fig. 2 of Ref. 13. The island size for the lowest CO partial pressure (the ‘clean’ case) is only a lower bound for $L_{1/2}$, since the first monolayer coalesces prior to second layer nucleation. The full symbols show the variation of the additional step edge barrier $\Delta E_S$ with $p_{CO}$. The data points represented by full circles are determined by use of equation (13). Due to the applied CO partial pressure, the additional step edge barrier increases dramatically from 0.12 eV to 0.36 eV. For the calculation, $\alpha$ was adjusted between 1/18 and 1/15 to account for the island geometry (compare to Fig. 1 of Ref. 13).

The results are compared to the step edge barrier obtained from the TDT theory. We have adapted their expression for the nucleation rate on a circular island (Eq.(3) of Ref. 5) to the notation of the present paper, which yields

$$1/\nu' = \left(\frac{12 \ln 2}{\gamma FN\nu \alpha^4 L_{1/2}^2} - \frac{52\alpha^2 L_{1/2}^2}{49 \nu^2} \right)^{1/2} - \frac{12 \alpha L_{1/2}}{7 \nu}.$$  

(35)

A reasonable choice for the capture number in this case is $\gamma = 3$. The resulting data is shown in Fig. 1 as full triangles. It is obvious that the TDT approach seriously underestimates the magnitude of the step edge barrier for large barriers; for example, for $p_{CO} = 1.85 \times 10^{-9}$ mbar the TDT formula yields $\Delta E_S = 0.28$ eV instead of 0.36 eV. We note that the strong barrier condition $\nu/\nu' > L$ is valid only for the CO partial pressures in excess of $1 \times 10^{-10}$ mbar, hence the barrier obtained using the LAM can be trusted only for these pressures. Attempts to improve the
estimates for small barriers using the upper bound (13) on the nucleation rate result in negative values for \( \nu' \), which shows that the bound is too rough to be useful.

We still need to address the consistency of our assumption that \( i^* = 1 \). In fact, at 400 K a Pt-dimer may not be considered to be a stable nucleus, because Pt-dimer breaking energies on Pt(111) obtained in experiment[3] and calculation\(^\ddagger\) vary from 0.49 eV to 0.81 eV. It is likely that at 400 K a trimer is a stable nucleus. At this temperature, the condition \( \tau_{tr} \ll \tau_{\text{dis}} \ll \Delta t \cdot (\tau_{tr}/\tau) \) for the scaling regime III of Section II C is fulfilled. For example, for the largest CO partial pressure and assuming a dimer breaking energy of 0.65 eV one obtains with the other values above \( \tau_{tr} = 1.4 \times 10^{-6} \text{ s}, \tau_{\text{dis}} = 1.9 \times 10^{-5} \text{ s} \) and \( \Delta t \cdot (\tau_{tr}/\tau) = 2.4 \times 10^{-3} \text{ s} \). Unfortunately the nucleation rate in regime III depends explicitly on the (unknown) dimer dissociation time, and therefore the expression (13) cannot be used for a quantitative analysis. Since nucleation on a top terrace is more difficult for \( i^* > 1 \) compared to \( i^* = 1 \), and at a given island size a more efficient step edge barrier is necessary for nucleation to occur, the step edge barrier obtained under the assumption \( i^* = 1 \) is only a lower bound.

We conclude, therefore, that the step edge barriers presented in Fig. 1 for pressures \( p_{\text{CO}} > 10^{-10} \text{ mbar} \) are lower bounds on the true values. For smaller pressures this need no longer be true, because our expression (13) underestimates the nucleation rate. For the data point corresponding to ‘clean’ growth (\( p_{\text{CO}} = 5 \times 10^{-12} \text{ mbar} \)) the situation is further complicated by the fact that the measurement yields only a lower bound on \( L_{1/2} \). Therefore at this point a direct comparison with other measurements[4] and calculations[5] of the additional barrier for clean steps on Pt(111) is not possible.

### IV. THE SIZE OF THE TOP TERRACE OF A WEDDING CAKE

In this section we apply the LAM to the growth of multilayer films in the “wedding cake” regime[4, 5]. Wedding cakes are pyramidal mounds of fixed lateral size which grow on the template of the first layer islands. They constitute the typical growth morphology under conditions of strong step edge barriers in the sense of Section II A. In the limit of infinite step edge barriers (\( \ell_{ES} \rightarrow \infty \)) the wedding cakes have a characteristic pointed shape which can be deduced from the observation[6] that the coverages of the exposed layers follow a Poisson distribution. When \( \ell_{ES} \) is finite but large the overall shape remains unchanged, however the pointed tip is replaced by a flat top terrace, whose typical size \( L_{\text{top}} \) directly reflects the strength of the step edge barriers[3, 6].

For an order of magnitude estimate it suffices to note that the approximate reproduction of the mound shape after the growth of an additional layer requires on average one nucleation event per top terrace and deposited monolayer, and therefore

\[
\omega(L_{\text{top}})/F \approx 1. \tag{36}
\]

The purpose of this section is to refine this argument and to develop a simple analytic model for the size distribution of top terraces. A detailed comparison with growth experiments on Pt(111)[6, 14] will be carried out in Section IV B, while extensions and modifications of the theory are discussed in Sections IV C and IV D.

#### A. Model for the dynamics of the top terrace

Any degree of interlayer transport couples the growth of all atomic layers[28]. However, the observation[15, 14] that for strong barriers the shape is affected only near the top of the wedding cake suggests that the main features can be captured in a model which decouples the growth of the top terrace from the rest of the structure. This is achieved most simply by assuming that the top terrace grows on a base terrace of fixed size \( \Lambda \), which is bounded by a step with an infinite edge barrier. Then all atoms landing on the base terrace or on the top terrace contribute to the growth of the latter, and its size evolves according to

\[
L(t) = \sqrt{Ft} \Lambda = \sqrt{\theta} \Lambda, \tag{37}
\]

where time \( t \) and coverage \( \theta = Ft \) are counted from the event of nucleation. The interpretation of \( \Lambda \) as the size of the base terrace should not be taken too literally, since we will allow for \( L \) to become larger than \( \Lambda \); rather, \( \Lambda \) sets the scale of the top terraces and will eventually be fixed self consistently. In principle the constraint \( L \leq \Lambda \) could be built into the growth law for \( L(t) \), but we have found that this does not improve the agreement with the experimental data to be presented in Section IV B. An example of such a modified growth law will be briefly discussed in Section IV D.

The growth law (37) holds until a new top terrace nucleates on the previous one, at which point \( L \) is reset to 0. The growth is assumed to be deterministic, which implies that fluctuations in the deposition and diffusion events on
the terrace are ignored. At least for sufficiently large terraces these should be negligible compared to the fluctuations in the times between subsequent nucleation events, which are taken into account explicitly. The probability for no nucleation to occur up to time $t$ (coverage $\theta = Ft$) is

\[ P_0(\theta) = \exp[-\int_0^t dt' \omega(L(t'))] = \exp \left[ -\frac{2}{k + 2} \Omega \Lambda^{k+2}/2 \right]. \quad (38) \]

Here the general expression for the nucleation rate as a function of island size and the relation for the time dependence of $L$ have been used. The distribution $P(\theta)$ of coverages between subsequent nucleation events is then given by $P(\theta) = -dP_0/d\theta$. To fix the value of $\Lambda$ we observe that, in order for the mound morphology to be reproduced after the growth of one layer, the mean of $P(\theta)$ should equal unity. This implies the condition

\[ \int_0^\infty d\theta \theta P(\theta) = \int_0^\infty P_0(\theta) = 1. \quad (39) \]

Inserting (38) we find

\[ \Lambda = \left( \frac{k + 2}{2} C_k \right)^{1/k} \Omega^{-1/k} \quad (40) \]

where

\[ C_k = \left[ \Gamma((k + 4)/(k + 2)) \right]^{(k+2)/2} \]

and $\Gamma$ denotes the $\Gamma$-function. For example, in the case $k^* = 1$ we have $k = 5$ and $\Omega = \alpha^3 F/\nu'$ and (40) yields

\[ \Lambda = 1.193 \cdot \alpha^{-3/5} (\nu'/F)^{1/5}. \quad (42) \]

It is plausible (and can be checked by a formal argument) that the probability $Q(L)$ of finding a top terrace of size $L$ is proportional to the probability that no nucleation has occurred up to coverage $\theta = (L/\Lambda)^2$. Using the expression (38) and transforming variables from $\theta$ to $L$ using (37) we find

\[ Q(L) = (d\theta/dL)(\theta)^{-1} P_0(L^2/\Lambda^2) = \frac{2L}{\Lambda^2} \exp[-C_k(L/\Lambda)^{k+2}]. \quad (43) \]

Here the condition $\langle \theta \rangle = 1$ has been enforced through the relation (40).

The distribution increases linearly for small $L$ and is rather abruptly cut off at $L \approx \Lambda$ (see Fig. 2). Its moments can be expressed in terms of $\Gamma$-functions. In particular, the mean size of the top terrace is given by

\[ \langle L \rangle/\Lambda = \frac{2}{3} \frac{\Gamma((k + 5)/(k + 2))}{\Gamma((k + 4)/(k + 2))^{3/2}}. \quad (44) \]

For $k \to \infty$ the factor on the right hand side approaches $2/3$, which corresponds to a linear distribution $Q(L) = 2L/\Lambda^2$ with a sharp cutoff at $L = \Lambda$. Already for $k = 5$ the ratio $\langle L \rangle/\Lambda \approx 0.692$ is very close to $2/3$. Another consequence of the skewed shape of $Q(L)$ is that the most probable value $L_{\text{max}}$ is considerably larger than the mean, and is generally given by

\[ L_{\text{max}}/\Lambda = (k + 2)^{-1/(k+2)} \Gamma((k + 4)/(k + 2))^{-1/2}. \quad (45) \]

For $k = 5$, $L_{\text{max}}/\Lambda \approx 0.80$, and $L_{\text{max}}/\Lambda \to 1$ for $k \to \infty$.

**B. Multilayer growth on Pt(111)**

The model for the dynamics of the top terrace is substantiated by its application to mound growth on Pt(111). As shown in Fig. 2, after deposition of 37.1 ML Pt with a deposition rate $F = 1.3 \times 10^{-2}$ ML/s in a partial pressure $p_{\text{CO}} = 1.9 \times 10^{-9}$ mbar of carbon monoxide at 440 K mounds form, which are built from terraces scattering slightly around the shape of an equal-sided hexagon. The differentiated representation (morphology appears illuminated from the left) of the scanning tunneling topographs allows to distinguish all atomic steps, in particular the steps bounding the top terrace and its base terrace. The applied CO partial pressure during growth results in a significant decoration
of step edges by CO molecules, while the equilibrium coverage of the terraces is negligible at 440 K (about $7 \times 10^{-3}$ ML [28]). As already mentioned in Section III E, the step decoration with CO gives rise to a significant increase in the additional step edge barrier [13].

The distributions of the sizes $L$ of the top terraces and $\Lambda$ of the base terraces determined for about 150 mounds are presented in Figure 2. The mean base terrace size in units of edge sites is $\langle \Lambda \rangle = 212$. The relatively narrow distribution of base terraces shown in Figure 2 supports our model assumption of a constant base terrace size. The mean top terrace size in units of edge sites is $\langle L \rangle = 142$. The ratio of the two averages $\langle L \rangle / \langle \Lambda \rangle = 0.67$. The most probable value $L_{\text{max}}$ is considerably larger than its mean and is found in the size interval $[0.78, 0.81] \langle \Lambda \rangle$.

For comparison with the growth model developed in the previous section a choice for the size of $i^*$ is necessary. As discussed in section III E, the scaling regime III with $i^* = 2$ most probably applies here. Consequently we perform the comparison of the shape of the size distribution for $i^* = 2$, i.e. $k = 6$ in [13]; note however that $\langle L \rangle$ depends rather weakly on $k$, and therefore the results assuming $i^* = 1$, $k = 5$ are almost identical. The experimental ratio $\langle L \rangle / \langle \Lambda \rangle = 0.67$ is in excellent agreement with the model prediction of $\langle L \rangle / \Lambda = 0.687$, and the range of experimental values for $L_{\text{max}}$ agrees very well with the model prediction $L_{\text{max}} = 0.81 \Lambda$. The figure also shows the analytic expression (43) for the distribution of top terrace sizes. Given the limited number of evaluated mounds, the agreement is quite satisfactory.

Due to the uncertainty in the dimer bond strength, for the quantitative estimate of $\nu'$ and $\Delta E_S$ we will assume $i^* = 1$; as discussed in Section III E this will provide a lower bound on the step edge barrier. Rearrangement of formula (42) yields

$$\nu' = 0.414 \cdot \alpha^3 F A^3. \quad (46)$$

Inserting the experimental deposition rate, choosing $\alpha = 1/12$ for equal-sided hexagons and a triangular lattice and $\langle \Lambda \rangle = 212$ as determined experimentally, we obtain for the hopping rate over step edges $\nu' = 1.32 \times 10^6 \text{s}^{-1}$. With the same assumptions as in section III E this translates into $\Delta E_S = 0.33 \text{ eV}$, in reasonable agreement with the step edge barrier obtained at 400 K and the same CO partial pressure in the analysis of second layer nucleation in Section III E. The agreement indicates that in both cases the CO concentration at the step edges was close to saturation, and supports the consistency of our two approaches to the determination of the additional step edge barrier from submonolayer islands and multilayer mounds.

C. The one-dimensional case

The considerations of Sections IV A and IV A are easily extended to one-dimensional islands. For an island of length $\ell$ the mean interval time between subsequent deposition events is $\Delta t = 1/F\ell$, while the residence time is $\tau = \ell/2\nu'$. Therefore the nucleation rate for strong step edge barriers and $i^* = 1$ is

$$\omega = \frac{\tau}{(\Delta t)^2} = \frac{F^3 \ell^3}{2\nu'}. \quad (47)$$

The time evolution for the size of the top terrace is now $\ell(t) = Ft\lambda = \theta \lambda$, with $\lambda$ denoting the length of the base terrace, and the probability $P_0(\theta)$ that no nucleation event has taken place after a coverage $\theta$ is

$$P_0(\theta) = \exp[-(F\lambda^3/8\nu') \theta^4]. \quad (48)$$

As before, $\lambda$ is determined by the condition (33). This implies

$$\lambda = (\Gamma(1/4)^{4/3}/2^{5/3})(\nu'/F)^{1/3} \approx 1.75 (\nu'/F)^{1/3}. \quad (49)$$

To summarize, for $i^* = 1$ the size of the top terrace scales with the Ehrlich-Schwoebel length as $\ell_{ES}^{-1/3}$ in $1 + 1$ dimensions, and as $\ell_{ES}^{-1/5}$ in $2 + 1$ dimensions. This agrees with the results found in Refs. 15 and 25 through a less quantitative method.

D. Deterministic nucleation and other modifications

To assess the importance of the fluctuations in the nucleation times, we now consider a model where nucleation occurs at fixed time intervals corresponding precisely to the growth of one monolayer. The base terrace size $\Lambda$ is determined
through the requirement that these nucleation times should correspond to the maximum of the distribution, i.e. rather than fixing the mean of $P(\theta)$ we fix the position of its peak. Noting that $P(\theta) = -dP_0/d\theta = F^{-1}\omega P_0$, the condition $dP/d\theta = 0$ for the maximum can be written as
\[
F \frac{d\omega}{d\theta} = \omega^2, \tag{50}
\]
where the nucleation rate (21) has been expressed in terms of the coverage using (37). Solving (50) and setting the corresponding coverage to unity yields
\[
\Lambda = \left(\frac{k}{2}\right)^{1/k} \Omega^{-1/k}. \tag{51}
\]
The numerical coefficients in (40) and (51) coincide within a few percent for $5 \leq k \leq 8$. Thus for most purposes the simpler relation (51) can be used. Similarly for the one-dimensional case with $i^* = 1$ the deterministic approach yields
\[
\Lambda = 6^{1/3} (\nu'/F)^{1/3} \approx 1.82 (\nu'/F)^{1/3}, \tag{52}
\]
very close to (49).

V. CONCLUSIONS

The main purpose of this paper has been to establish some quantitatively accurate relations between microscopic parameters and large scale morphology for homoepitaxial growth in the presence of destabilizing step edge barriers, and to demonstrate their usefulness for the well-studied case of Pt/Pt(111). Perhaps surprisingly, we found that a quantitative analysis of nucleation is simpler with strong step edge barriers than without them: Due to the homogeneity of the adatom occupation probability, and the relation $p_{\text{nuc}} = p_2$, our expression (9) for the nucleation rate is exact in the strong barrier regime for any island shape. It would be most desirable to obtain exact results also for intermediate and weak barriers as well as for reversible aggregation, but for the reasons described in Sections II B and II C such an extension is far from straightforward.

On a conceptual level, the reasons for the failure of the rate equation ansatz (1) in the present problem need to be better understood. We have identified one regime in the case $i^* = 2$ in which our analysis agrees with the rate equation theory (see Section II C); such a regime exists also for $i^* > 2$, but the precise conditions for the validity of (1) are not clear. In this context it is worth pointing out that the standard rate equation approach also fails in one-dimensional nucleation (39–41). This suggests that the rate equation treatment may generally be expected to be problematic in situations involving low-dimensional or confined geometries.

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APPENDIX A: CALCULATION OF $P_{N+1}$

Here we compute the probability $p_{n+1}$ of finding $n+1$ (noninteracting) adatoms simultaneously on the island. Denote by $t_i$ the time interval between the arrivals of atoms $i$ and $i+1$, and by $\tau_i$ the residence time of atom $i$, with $i=1,\ldots,n$. The first atom arrives at time $t=0$, the second at time $t=t_1$ and so on. For all $n$ atoms to still be on the island when the $(n+1)$st atom arrives, the residence times have to satisfy the conditions $\tau_i > t_i + t_{i+1} + \ldots + t_n$. The $t_i$ and $\tau_i$ are exponential random variables with mean $\Delta t$ and $\tau$, respectively. Thus

$$p_{n+1} = (\Delta t)^{-n} \prod_{i=1}^{n} \int_0^\infty dt_i \cdot e^{-t_i/\Delta t} \prod_{i=1}^{n} \int_{t_i+t_{i+1}+\ldots+t_n}^\infty d\tau_i \cdot e^{-\tau_i/\tau} =$$

$$= (\Delta t)^{-n} \prod_{i=1}^{n} \int_0^\infty dt_i \cdot e^{-t_i/\Delta t} \prod_{i=1}^{n} e^{-(t_i+t_{i+1}+\ldots+t_n)/\tau} = (\Delta t)^{-n} \prod_{i=1}^{n} \int_0^\infty dt_i \cdot \exp[-t_i(1/\Delta t + i/\tau)] =$$

$$= \prod_{i=1}^{n} (1 + i\Delta t/\tau)^{-1}. \quad (A1)$$

For $\tau \ll \Delta t$ this reduces to

$$p_{n+1} \approx \frac{1}{n!} \left( \frac{\tau}{\Delta t} \right)^n. \quad (A2)$$

APPENDIX B: CRITICAL ISLAND SIZE FOR $i^* = 2$

In the different regimes described in Section [11], the critical island size for second layer nucleation is given by the expressions

$$L_c \sim \left( \frac{\nu'}{F} \right)^{2/7} \left( \frac{\nu^2 \tau_{\text{dis}}}{\nu'} \right)^{-1/7} N^{-1/7} \quad \text{(regime I)} \quad (B1)$$

$$L_c \sim \left( \frac{\nu'}{F} \right)^{1/5} N^{-1/10} \quad \text{(regime II)} \quad (B2)$$

$$L_c \sim \left( \frac{\nu'}{F} \right)^{1/4} (\nu \tau_{\text{dis}})^{-1/8} N^{-1/8} \quad \text{(regime III)} \quad (B3)$$

and for general $i^*$ the nucleation rate [19] for regime II yields

$$L_c = \left( \frac{4 + 3i^*}{2\alpha^2 + 2} \right)^{1/(4+3i^*)} \left( \frac{\nu'}{F} \right)^{i^*/(4+3i^*)} N^{-1/(4+3i^*)}. \quad (B4)$$

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FIG. 1. Critical island size $L_{1/2}$ (open circles) and the resulting additional step edge barrier $\Delta E_S$ (full symbols) as a function of CO partial pressure. Full circles were calculated according to the LAM formula (34), while full triangles were obtained using the TDT formula (35).

FIG. 2. Size distribution of top terraces. The full line shows a histogram obtained from the evaluation of 145 mounds, and the thick dotted line shows the (appropriately normalized) theoretical prediction (43). The thin dashed line is included to illustrate the narrowness of the distribution of base terraces.

FIG. 3. Typical STM image of mounds appearing on the surface after the deposition of 37.1 ML Pt/Pt(111) in a partial CO pressure of $1.9 \times 10^{-9}$ mbar. Eight top terraces and the corresponding base terraces can be seen.
