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Low-temperature shape relaxation of two-dimensional islands by edge diffusion

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We present a precise microscopic description of the limiting step for low-temperature shape relaxation of two-dimensional islands in which activated diffusion of particles along the boundary is the only mechanism of transport allowed. In particular, we are able to explain why the system is driven irreversibly towards equilibrium. Based on this description, we present a scheme for calculating the duration of the limiting step at each stage of the relaxation process. Finally, we calculate numerically the total relaxation time as predicted by our results and compare it with simulations of the relaxation process.

I. INTRODUCTION

The understanding, description, and control of structures at the nanometer scales is a subject of interest from the fundamental and applied points of view.[1,2] From the fundamental point of view, there is a large literature[3,4] concerning the growth of crystals and their shape. Yet, while the description of the equilibrium shape is rather clear, the dynamic description of crystal growth is still not well understood. In particular, we lack a complete understanding of the time scales involved in the relaxation process, and the mechanisms which irreversibly conduce the island to its equilibrium shape.

In this work, we study the shape relaxation of two-dimensional islands by boundary diffusion at low temperatures. The typical size of the islands we will be concerned with consists of a few thousand atoms or molecules, corresponding to islands of a few nanometers. The model we consider is the same as the one studied in Ref. 5, where two mechanisms of relaxation, depending on temperature, were pointed out: At high temperatures, the classical theory developed by Herring, Mullins, and Nichols[6] appears to describe adequately the relaxation process. In particular, it predicts that the relaxation time scales as the number of atoms to the power 2. However, at low temperatures, the islands spend long times in fully faceted configurations, suggesting that the limiting step of the relaxation in this situation is the nucleation of a new row on a facet. This assumption leads to the correct scaling behavior of the relaxation time on the size of the island, as well as the correct temperature dependence. Yet, it is unclear what drives the island towards equilibrium in this scenario.

In this paper we propose a detailed description of this low-temperature relaxation mechanism, and identify the event that drives the island towards its equilibrium shape. Based on our description, we construct a Markov process from which we can estimate the duration of each stage of the relaxation process. Finally, we use our result to determine the relaxation time of the islands and compare with simulation results.

The specific model under consideration consists of two-dimensional (2D) islands having a perfect triangular crystalline structure. A very simple energy landscape for activated atomic motion was chosen: the aim being to point out the basic of mechanisms of relaxation, and not to fit the specific behavior of a particular material. The potential energy E_p of an atom is assumed to be proportional to the number i of neighbors, and the *kinetic barrier* E_{act} for diffusion is also proportional to the number of *initial* neighbors before the jump, regardless of the *final* number of neighbors: $E_{act}=-E_p=i*E$ where E sets the energy scale ($E=0.1$ eV throughout the paper). Therefore the probability p_i per unit time that an atom with i neighbors moves is $p_i=\nu_0\exp[-i*E/k_bT]$, where $\nu_0=10^{13}$ s^{-1} is the Debye frequency, k_B is the Boltzmann constant and T the absolute temperature. Hence the average time in which a particle with i neighbors would move is given by

$$\tau_i=\nu_0^{-1}\exp[i*E/k_bT]. \tag{1}$$

The complete description of the model and of the simulation algorithm can be found in Ref. 5, where it was studied using standard kinetic Monte Carlo simulations. This simple kinetic model has only *one* parameter, the ratio E/k_BT. The temperature was varied from 83 to 500 K, and the number of atoms in the islands from 90 up to 20 000. The initial configurations of the islands were elongated (same initial aspect ratio of about 10), and the simulations were stopped when the islands were close to equilibrium, with an aspect ratio of 1.2. The time required for this to happen was defined as the relaxation time corresponding to that island size and temperature. Concerning the dependence of the relaxation time on the size of the island, two different behaviors depending on temperature were distinguished.[5] At high temperature, the relaxation time scaled as the number of atoms to the power 2, but this exponent decreased when temperature was decreased. A careful analysis showed that the exponent tends towards 1 at low temperature. The dependence of the relaxation time as a function of temperature also changes, the activation energy was 0.3 eV at high temperature and 0.4 eV at low temperature. In this context, it is important to define what we call a low-temperature: following Ref. 5, we denote by L_c the average distance between kinks on a infinite facet: we define the low-temperature regime as that in which $L_c \gg L$ where L is the typical size of our island, large facets are

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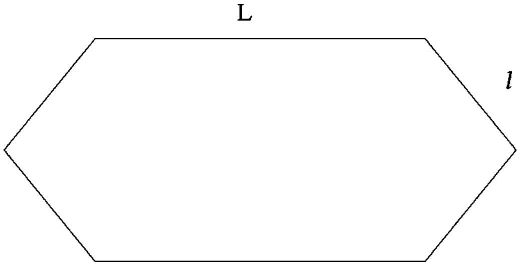

FIG. 1. Configuration of the island we will consider in the qualitative description as well as in the quantitative one.

then visible on the island. It was shown that $L_c = (a/2)\exp(E/2k_bT)$ where a is the lattice spacing.

The behavior of the relaxation time as a function of the temperature and N, the number of particles of the island, can be summed up with two equations corresponding to the high- and low-temperature regimes:

$$t^{HT}_{relaxation} \propto \exp[3E/k_bT]N^2 \quad \text{for} \quad N \gg L_c^2, \tag{2}$$

$$t^{LT}_{relaxation} \propto \exp[4E/k_bT]N \quad \text{for} \quad N \ll L_c^2. \tag{3}$$

Replacing the temperature dependent factors by a function of N_c the crossover island size [where $N_c = L_c^2 \propto \exp(E/k_bT)$], these two laws can be expressed as a unique scaling function depending on the rescaled number of particles N/N_c:

$$t_{relaxation} \propto \begin{cases} N_c^5 \left(\dfrac{N}{N_c}\right)^2 & \text{for } \dfrac{N}{N_c} \gg 1 \\ N_c^5 \dfrac{N}{N_c} & \text{for } \dfrac{N}{N_c} \ll 1 \end{cases},$$

so that the relaxation time[7] is a simple monotonous function of N/N_c, and the temperature dependence is contained in N_c. We will now focus on the precise microscopic description of the limiting step for relaxation in the low-temperature regime.

II. DESCRIPTION OF THE LIMITING PROCESS AT LOW TEMPERATURE

A. Qualitative description

During relaxation at low temperature, islands are mostly in fully faceted configurations. Let us, for instance, consider an island in a simple configuration given by Fig. 1. When L is larger than l, the island is not in its equilibrium shape (which should be more or less a regular hexagon). To reach the equilibrium shape, matter has to flow from the ''tips'' of the island (facets of length l in this case) to the large facets L. In this low-temperature regime there are very few mobile atoms at any given time, therefore this mass transfer must be done step by step: the initial step being the nucleation of a ''germ'' of two bound atoms on a facet of length L and then, the growth of this germ up to a size $L-1$ due to the arrival of particles emitted from the kinks and corners of the boundary of the island. Thus the germ grows, and eventually completes a new row on the facet.

This simple picture still leaves a basic question unanswered: the relatively faster formation of a new row on a small facet would lead the island further away from its equilibrium shape, and yet, we observe that this never happens. Indeed, sometimes a germ appears on a small facet but it eventually disappears afterwards, whereas the appearance of a germ on a large facet frequently leads to the formation of a new row, taking the island closer to its equilibrium shape.

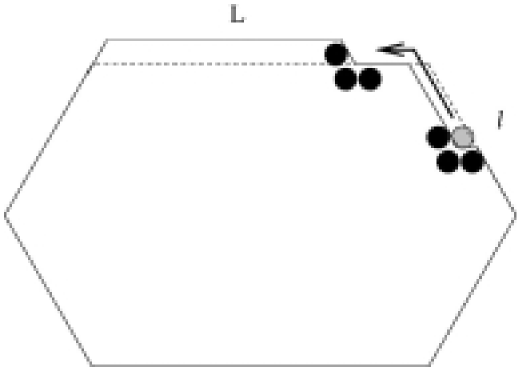

FIG. 2. The total energy of the island does not change when one particle leaves a kink on the small facet to go in the germ on the large facet.

These observations are at the root of irreversible nature of the relaxation, germs only grow and become stable on the large facet, so the island can only evolve to a shape closer to equilibrium. Yet, there is clearly no local drive for growth on large facets nor any mechanism inhibiting growth on small ones. In order to explain how this irreversibility comes about, we propose the following detailed description of the mechanism of nucleation and of growth of a germ.

First, to create a germ, two atoms emitted from the corners of the island have to encounter on a facet. The activation energy required for this event is obviously independent of whether it occurs on a large facet or on a small facet. Once there is a germ of two atoms on a facet, the total energy of the island *does not* change when a particle is transfered from a kink to the germ (three bonds are broken, and three are created), see Fig. 2. Clearly the same is true if a particle from the germ is transfered to its site of emission or any other kink. Thus germs can grow or decrease randomly without energy variations driving the process. An exception to this occurs if the particle that reaches the germ is the last one of a row on a facet; in that case, the energy of the system decreases by one binding energy E. The island is then in a configuration from which it is extremely improbable to return to the previous configuration. For this to occur, a new germ would have to nucleate (and grow) on the original facet. This event is almost impossible in the presence of the kinks of the first growing germ, which act as traps for mobile atoms. Thus, when a germ nucleates on a facet, it can grow or decrease without changing the energy of the island except if a complete row on a facet disappears, in which case it ''stabilizes.''

The scenario above explains why no new rows appear on small facets: when a germ grows on a small facet, since atoms come either from a small or a large facet, no complete row of a facet can disappear during the germ's growth, and thus the island never decreases its energy. On the other hand when the germ grows on a large facet, the germ might grow or decrease, but if the size of the germ reaches the size of the small facet, the energy of the system will decrease and the

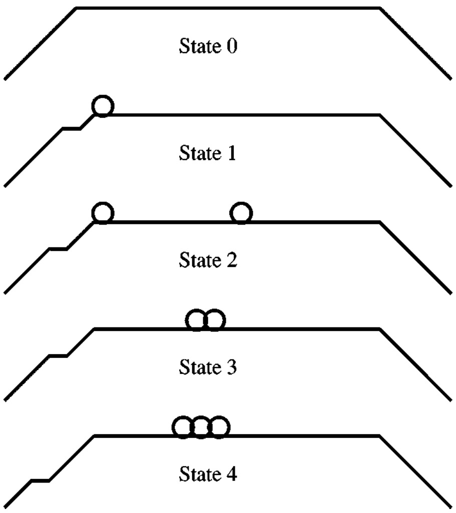

FIG. 3. Outline of the states considered in the Markov chain.

system has almost no chance to go back its previous shape. We believe that this is the microscopic origin of irreversibility in the relaxation of this system. It should be stressed that this scenario for the growth and stabilization of germs is different from usual nucleation theory, where the germ has to overcome a free energy barrier[8] to become stable.

This microscopic description also shows that the limiting step for this ''row by row'' relaxation mechanism is actually the formation on a large facet, of a germ of the size of the small facet. This fact allows us to estimate the duration of the limiting step at each stage of the relaxation process.

B. A quantitative description

Based on our description of the process, we propose a scheme for calculating the time required to form a stable germ, i.e., a germ of size *l*, on a facet of size *L*. As mentioned above, the appearance of this stable germ is the limiting step for the formation of a new row on that facet.

The idea is to describe the growth of the germ as a succession of different island states, and calculate the probability and the time to go from one state to another in terms of the actual diffusive processes occurring on the island surface. These states form a Markov chain, the future evolution of the system being essentially determined by the state of the system, independently of its previous behavior.

As a further simplification, we consider a simple fully faceted island in a elongated hexagonal shape whose facets are of length L and l, see Fig. 1; moreover, we normalize every length by the lattice spacing *a*.

The different states we consider are (see Fig. 3 also)

•state 0: there is no particle on the facets;

•state 1: one particle is on one end of a facet *L*;

•state 2: two particles are on the facet *L*: one of them is on one end of the facet, and the other one has diffused from an end;

•state 3: two particles are on the facet L but they are bonded together;

•state 4: three bonded particles are on the facet *L*;

. . .

•state *n*: $n-1$ bonded particles are on the facet *L*.

The goal of this calculation is to estimate the time to go from state 0 to state $l+1$. We treat the problem as a discrete time Markov chain. The unit time being τ_2, the typical time for a particle with two neighbors to move. This time is in fact the smallest relevant time of the system so that the operation of discretization does not affect the results. In the following, the time τ_i is the average time for a particle with *i* neighbors to move: $\tau_i=\nu_0^{-1}e^{i*E/kT}$. For clarity, we will use the term *time* for the discrete time of the Markov chain, and the term *real time* for the time of physical process. The obvious relation between the two time scales is: $\mathit{time}=\text{real time}/\tau_2$.

We define the parameter $\rho=\tau_2/\tau_3$. In the limit of small temperature, ρ is a very small quantity. Moreover, one can easily check that $\rho=\exp(-E/kT)=2/L_c^2$ where L_c is the average distance between kinks defined in the first section. So that the condition $L_c \gg L$ (low-temperature regime) could be written as: $\sqrt{\rho}L \ll 1$ or $\rho L \ll 1/L < 1$.

Denote by α_i the probability for the system in state i to stay in the state i the following step, p_i the transition probability for system in state i to go to state $i+1$, and q_i the transition probability for the system to go into state $i-1$. We have now to evaluate the different quantities α_i, p_i, and q_i in terms of the diffusive processes that take place on the island's boundary.

We first evaluate the quantities p_1,q_1, and α_1. Let us assume that the states 0 and 2 are absorbent; the average time n_1 needed to leave state 1, corresponds to the average real time a particle stays on a facet starting on one of its edges, which act as traps. Since the particle performs a random walk, this can be readily calculated to be $L\tau_2$. So we should have

$$n_1=\frac{1}{1-\alpha_1}=L. \tag{4}$$

Moreover, the probability to go to state 2 is the probability that a new particle leaves a kink and reaches the facet while the first particle is still on the facet, we calculate this probability in Appendix A where we find

$$P=1-\left[\frac{2\sinh[2\sqrt{\rho}(L-1)]}{\sinh[2\sqrt{\rho}L]}-\frac{\sinh(2\sqrt{\rho}(L/2-1))}{\sinh(2\sqrt{\rho}L/2)}\right]. \tag{5}$$

We expand expression Eq. (5) for small ρ keeping the first term:

$$P=2\rho(L-1)+o(\rho). \tag{6}$$

We could also calculate the probability b_1, that the system in state 1 eventually reaches state 2 as

$$b_1=\alpha_1 b_1+p_1. \tag{7}$$

Thus $b_1=p_1/(1-\alpha_1)$, and using $p_1+\alpha_1+q_1=1$ we find

$$p_1=\frac{P}{L}\simeq 2\rho\frac{L-1}{L}+o(\rho), \tag{8}$$

$$\alpha_1=1-1/L, \tag{9}$$

$$q_1=\frac{1}{L}-\frac{P}{L}\simeq\frac{1}{L}-2\rho\frac{L-1}{L}+o(\rho). \tag{10}$$

We can do the same with state 2, knowing that the probability for two particles to stick (state 3) is λ/L, where $\lambda = [(\cosh \pi + 1)/\sinh \pi]\pi$ (the calculation of this probability is carried out in Appendix B). The time to leave state 2 is κL, where κ is a numerical constant given by $\kappa = (4/\pi^2)\Sigma_{k=1}^{\infty}[1/(1+4k^2)][2-1/(2k+1)]$ (see Appendix C). Thus we obtain

$$p_2 = \frac{\lambda}{\kappa L^2}, \tag{11}$$

$$\alpha_2 = 1 - \frac{1}{\kappa L}, \tag{12}$$

$$q_2 = \frac{1}{\kappa L} - \frac{\lambda}{\kappa L^2}. \tag{13}$$

In order to obtain a chain which can be treated analytically, we assume that the probability to go from state 3 to state 4, is the same as the probability to go from state 4 to state 5 and, in general, that the probabilities to go from state i to state $i+1$ are $p_i = p_{i+1} = p$ for $i \geqslant 3$. Similarly, we assume that $\alpha_i = \alpha_{i+1} = \alpha$ for $i \geqslant 3$ and $q_i = q_{i+1} = q$ for $i > 3$.

To calculate the probabilities p, q, α, in Appendix D we have calculated the average real time $t_{p,q,\alpha}$ to go from state i to state $i+1$ assuming the average distance between kinks and the germ is $L/2$: $t_{p,q,\alpha} = L/4 * \tau_3 + L(L-2)/4 * \tau_2$. Moreover, since $p = q$, we can calculate p, q, and α:

$$p = 2\rho/L - \frac{2(L-2)}{L}\rho^2 + o(\rho^2), \tag{14}$$

$$\alpha = 1 - \frac{4\rho}{L} + \frac{4(L-2)}{L}\rho^2 + o(\rho^2), \tag{15}$$

$$q = 2\rho/L - \frac{2(L-2)}{L}\rho^2 + o(\rho^2). \tag{16}$$

When two particles are bonded on the facet (state 3), the probability to go to state 2 should practically be equal to q, we will assume this to be the case.

So far, we have omitted the possibility that the germ can also nucleate on a small facet l. To take this into account, we have to consider new states:

•state -1: one particle is on the facet l on one of its edges;

•state -2: two particles are on the facet l: one of them is on the edge of the facet, and the other has diffused from an edge;

•state -3: two particles are on the facet l but they are bonded;

•state -4: three bonded particles are on the facet l;

. . .

•state $-l$: $l-1$ bonded particles are on the facet l.

As discussed above, if the system arrives to state $-l$, a row on a small row is completed, which is not an absorbent state, and since this row cannot grow any further the system can only go back to state $-l+1$ or stay in state $-l$.

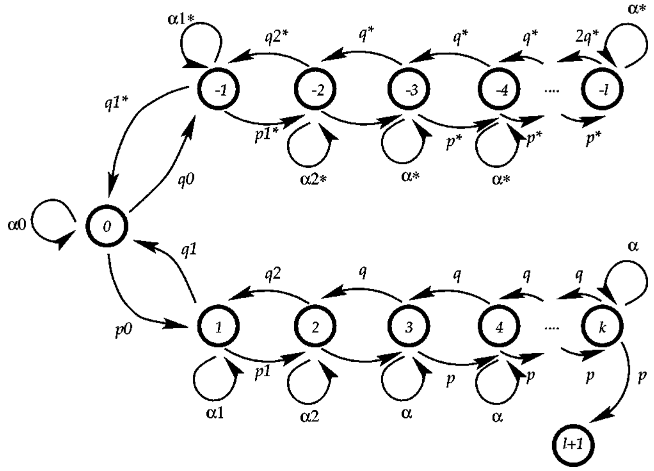

FIG. 4. Diagram of the entire Markov chain with the two branches: the upper one for the germs growing on a small facet and the other one for the germs growing on the large one, state $l+1$ is the only absorbing state.

The different probabilities of transition from one state to another in this branch of the chain are the same as the ones calculated before, replacing L by l. Thus we have $q_{-i} = p_i(L \Rightarrow l)$, $p_{-i} = q_i(L \Rightarrow l)$, and $\alpha_{-i} = \alpha_i(L \Rightarrow l)$ for $i \geqslant 1$ except for the state $-l$, where we always have $\alpha_{-i} = \alpha(L \Rightarrow l)$, but, $p_{-l} = 2 * q(L \Rightarrow l)$. In the following, we will use the notation: $p_i^* = p_i(L \Rightarrow l)$, the values of p_i where we have replace L by l.

To complete the calculation, we now have to determine p_0, q_0 and α_0. The average real time the system stays in state 0, assuming states 1 and -1 are absorbent, is almost $\tau_3/2$ if we take into account that there are *two* kinks, one at each end of the facet. The probability that the germ nucleates on the facet L is simply $L/(L+2l)$. From this we deduce:

$$p_0 = 2\frac{L}{L+2l}\rho, \tag{17}$$

$$\alpha_0 = 1 - 2\rho, \tag{18}$$

$$q_0 = 2\frac{2l}{L+2l}\rho. \tag{19}$$

The diagram of the entire Markov chain is then given by Fig. 4. And we will calculate the time to go from state 0 to state $l+1$.

The state $l+1$ is absorbent (as discussed above, when the size of the germ reaches l on a large facet, the system cannot go back to the initial state). Let us call n_i the average time to go from state i to state $l+1$. We can write

$$n_{-l} = 1 + 2q^* n_{-l-1} + \alpha^* n_{-l}, \tag{20}$$

$$n_{-k} = 1 + q^* n_{-k-1} + \alpha^* n_{-k} + p^* n_{-k+1}, \tag{21}$$

$$\text{with} \quad 3 \leqslant k \leqslant l \tag{22}$$

$$\cdots$$

$$n_{-2} = 1 + q_2^* n_{-1} + \alpha_2^* n_{-2} + p_2^* n_{-3}, \tag{23}$$

$$n_{-1} = 1 + q_1^* n_0 + \alpha_1^* n_{-1} + p_1^* n_{-2}, \tag{24}$$

$$n_0 = 1 + q_0 n_{-1} + \alpha_0 n_0 + p_0 n_1, \tag{25}$$

$$n_1 = 1 + q_1 n_0 + \alpha_1 n_1 + p_1 n_2, \tag{26}$$

$$n_2 = 1 + q_2 n_1 + \alpha_2 n_2 + p_2 n_3 \tag{27}$$

$$\cdots$$

$$n_k = 1 + q n_{k-1} + \alpha n_k + p n_{k+1}, \tag{28}$$

$$\text{with } 3 \leqslant k \leqslant l-1. \tag{29}$$

The boundary condition for this process is $n_{l+1}=0$. The calculation of n_0 is quite straightforward but tedious, it is carried out in Appendix E. We find that in the limit of small temperatures, the typical real time needed to nucleate a germ of size l on a facet of size L is given by

$$\tau(L,l) \approx \frac{\tau_3^2}{\tau_2} \frac{(L+2l)}{4L(L-1)} \left[\left(\frac{L}{\lambda} - 1 \right)(l-1) + 1 \right], \tag{30}$$

where we have kept only the most relevant term at low temperatures.

III. ESTIMATION OF THE RELAXATION TIME

Scaling laws

In this section we calculate the typical time required for an island to relax from an initial out of equilibrium shape. We assume that at all times, the instantaneous shape of the island can be characterized by the lengths L and l of its long and short facets, respectively. Then, following the discussion in the previous sections, a new row of particles will appear on a long facet after a time $\tau(L,l)$. Thus, calling $v(L)$ the normal speed of the large facet and taking the particle size as our unit distance, we have

$$v(L) \approx \frac{1}{\tau(L,l)} \approx \frac{4\tau_2 L(L-1)}{\tau_3^2 (L+2l) \left[\left(\frac{L}{\lambda} - 1 \right)(l-1) + 1 \right]}. \tag{31}$$

The scaling properties of the relaxation time can be deduced by noticing that the length scales involved scale as $N^{1/2}$, where N is the number of atoms of the island. Thus we renormalize the lengths by $x \rightarrow x' = N^{-1/2} x$. Then, to scale out the size dependence as N grows, one must rescale time by $t \rightarrow t' = t N^{-1}$. This is the result obtained in Ref. 5: at low temperature, the relaxation time is proportional to the number of the atoms of the island. But, as we expect our results for the time required to complete a row at each stage, as given in Eq. (E10), to be relatively accurate, we can go beyond the scaling properties and use it to calculate numerically the time required for the complete relaxation process, including the corrections arising from the lower-order terms.

In what follows, we establish the differential equations which permit the calculation of the full relaxation time of an island. As mentioned above, we still consider the simple island of Fig. 1, where $v(L)$ is the normal speed of the facet L, and $v(l)$ that of the facet l. We now consider L and l as continuous variables, which considerably simplifies the calculation.

Conservation of the matter imposes the relation

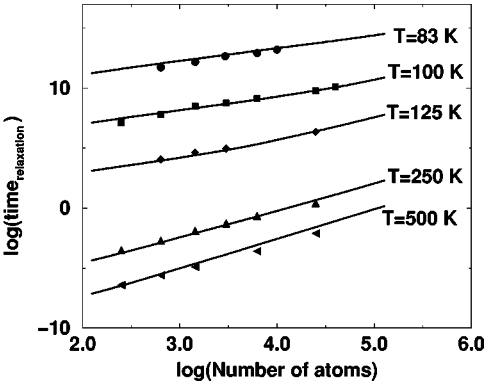

FIG. 5. Size dependence of the relaxation time for different temperatures in log-log bases. Filled points have been obtained by Monte Carlo simulations whereas the solid lines have been obtained by integration of the system (35) and (36). The agreement of the two analyses is almost perfect.

$$L v(L) + 2 l v(l) = 0. \tag{32}$$

Moreover, we can find geometric relations between $L, l, v(L), v(l)$:

$$v(L) = \sqrt{3}/2 \frac{dl}{dt}, \tag{33}$$

$$v(l) = \sqrt{3}/4 \left(\frac{dl}{dt} + \frac{dL}{dt} \right). \tag{34}$$

So finally we find

$$\frac{dl}{dt} = \frac{2}{\sqrt{3}} \frac{1}{\tau(L,l)}, \tag{35}$$

$$\frac{dL}{dt} = -\frac{2}{\sqrt{3}} \left(\frac{L}{l} + 1 \right) \frac{1}{\tau(L,l)}. \tag{36}$$

To integrate these equations numerically: we use Eq. (E10), and for $p1, q1$, and α_1 the exact estimation using Eq. (A9), as well as the explicit values of the quantities q_i, α_i, and p_i we have found: Eqs. (11)–(19). We start the integration from an island of aspect ratio of $R=10$, and stop it when the aspect ratio is $R=1.2$. Aspect ratios are explicitly calculated as

$$R = \frac{r_x}{r_y}, \tag{37}$$

$$r_x^2 = \frac{1}{S} \int \int_{Island \ \ Surface} (x - x_G)^2 dx dy, \tag{38}$$

$$r_y^2 = \frac{1}{S} a \int \int_{Island \ \ Surface} (y - y_G)^2 dx dy, \tag{39}$$

$$S = \int \int_{Island \ \ Surface} dx dy, \tag{40}$$

where x_G and y_G give the position of the center of gravity of the island. We report in Fig. 5 the relaxation time as a function of N, the number of particles of the island in a log-log plot. We find a good quantitative agreement between the simulations and our predictions except at the highest temperatures (see below).

IV. SUMMARY AND DISCUSSION

We have considered the shape evolution of two-dimensional islands as a result of the nucleation of a germ on a facet which then grows or decreases due to single-particle processes. Then we recognized that the disappearance of a complete row is responsible for the stabilization of the germ, and that this is only feasible for germs growing on the large facets. This gives rise to an overall flux of particles from the small facets to the large facets which leads the shape of the island irreversibly towards equilibrium. Based on this description, we have recast the formation of stable germs, which is the limiting step for relaxation, into a Markov chain in which the transition probabilities are calculated in terms of the underlying diffusive processes taking place on the island's boundary. Solving this chain yields an estimate of the time of formation of a new row at each stage of the relaxation. Integrating our results we can obtain the relaxation time for the evolution of an island from an aspect ratio of 10 to an aspect ratio of 1.2, as a function of temperature and island size. Our results have a rather good quantitative agreement with those obtained from direct simulations of the system. At higher temperatures, multiple nucleation processes, the presence of many mobile particles on the island's boundary and the failure of our hypothesis $L_c \gg L$ (Sec. II B) invalidate our picture and the relaxation becomes driven by the coarsed grained curvature of the boundary, which leads to Mullins classical theory.

The description of the simple model considered in this work is certainly not exact and there are other effects that could be taken into account. Perhaps the most important effect we have overstepped at low temperatures, is related to our assumption that after the germ stabilizes a single new row is formed on the large facet. The differential equations for the evolution of the island were derived from this assumption. It is clear that this is not correct: Our estimation of the time required to stabilize a germ starts from a fully faceted configuration, and once a complete row on a small facet disappears the germ becomes stable and a full row on the large facet can be formed. Once this row is finished, it is very unlikely that the island will be in a fully faceted configuration again, leaving at least an extra kink on the boundary. This gives rise to extra sources and traps for mobile particles, which might have affected the relaxation rate. Another issue is our characterization of the faceted island with only two facets sizes: a more detailed characterization may be relevant especially in the early stages of relaxation. It is clear that more accurate models for specific systems can also be constructed. These could take into account the dependence of the edge-diffusion coefficients on the orientation of the facet, as well as the dependence of emission rates on the local geometry. Such dependences have been studied, for example, by Ref. 9. In terms of the elements of description we use, inclusion of these effects would be achieved by changing the values of τ_2 (diffusion time) and τ_3 (emission time from kinks and corners) depending on the orientation of the facets involved in each event. Thus the nucleation time would depend on the facet upon which it happens. Such a dependence of the nucleation time may drive the island toward a nonregular hexagon equilibrium shape,[10] and would reproduce the phenomenology of a larger variety of materials. These changes will affect the temperature dependent prefactors in our results, as these depend on the temperature through τ_2 and τ_3. However, the size dependence of the nucleation time and of the relaxation time, which is where the departure from Mullin's theory is evidenced, would stay the same.

From a more general point of view, only the diffusion of particles along the perimeter of islands has been taken into account in this work. In real systems, other mechanisms can contribute to the transport of the matter which leads to relaxation: volume diffusion and transport through the two-dimensional gas of particle surrounding the island. Volume diffusion is usually a much slower process than the other two, and can usually be neglected safely. On the other hand, it is well known that edge diffusion is more efficient for short trips whereas transport through the 2D gas is faster on long distances. Following Pimpinelli and Villain in Ref. 4 (p. 132), a characteristic length r_1 beyond which edge diffusion is less efficient than transport through the gas can be evaluated: $r_1 \approx \sqrt{D_s \tau_v}$ where D_s is the edge diffusion coefficient and $1/\tau_v$ the probability per unit time a given particle leaves the island. So that our assumptions should be valid for islands with a number N of particles such that $N \ll D_s \tau_v$. Since the activation energy for edge diffusion is smaller than the activation energy for evaporation, r_1 is a decreasing quantity with temperature, and we expect r_1 to be very large at low temperature. Thus, this mechanism is essentially irrelevant in the description of the evolution of nanometer structures at low temperatures. Moreover, recent experimental results[11] have shown that supported Ag two-dimensional islands relax via atomic diffusion on the island perimeter, without significant contribution from exchange with the two-dimensional gas.

Finally, our results are to be compared with a recent theoretical study[12] concerning the relaxation of three-dimensional crystallites. This study also points out two relaxation regimes as a function of temperature. At high temperature the relaxation scales in accordance with the results derived from Mullins' theory, whereas at low temperature the relaxation time becomes an exponentional function of the size of the crystallites. So that the effects of lowering the temperature are qualitatively different for two-dimensional and three-dimensional crystallites: In two dimensions, lowering the temperature decreases the strength of the dependence of the relaxation time as a function of the size of the crystallites (as it crosses over from a N^2 dependence to a N dependence), whereas it increases this the strength in three dimensions. In both cases, the limiting step is the nucleation of a germ on a facet: a unidimensional germ in two dimensions, and a two-dimensional germ in three dimensions. The difference stems from the fact that in the two-dimensional case, the activation energy for the creation of the germ does not depend on the size of the island, it is always constant, $4E$, and it stabilizes when a row on a small facet has been removed. In the three-dimensional case, this activation energy depend on the size of the crystallite. The transfer of a particle from a tip of the crystallite to the germ has a gain in volume energy (depending on the size of the islands) and a loss in edge energy of the germ (depending on the size of the germ). Summing these two terms, an energy barrier proportional to the size of the crystallite appears for the creation of a stable germ. The exponential behavior of the relaxation time as a function of N is a consequence of this energy barrier dependence. Finally, we believe that the overall picture presented here, while still oversimplified, seems to be complete enough to provide a general picture of the processes leading to the shape relaxation of two-dimensional islands at low temperatures.

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APPENDIX A: CALCULATION OF THE PROBABILITY TO HAVE TWO PARTICLES ON THE FACET

We calculate the probability P of having two particles on a facet with absorbing boundaries, knowing that at time $t=0$, one particle is on one edge of the facet (abscissa 1), and that the other particle can appear on the facet with a probability per unit time $1/\tau$. Relatively to our Markov chain, this probability is the probability the system in state 1 eventually reaches state 2.

We denote by $S(x,t)$ the probability that a particle on the facet at position x at time $t=0$ is still on the facet at time t. Then, $S(x,t)$ satisfies the usual diffusion equation

$$\frac{\partial S(x,t)}{\partial t}=D\frac{\partial^2 S(x,t)}{\partial x^2}. \tag{A1}$$

This equation is to be solved with the conditions: $S(x,0)=1$ for every $x\in]0,L[$ (i.e., we are sure to find the particle on the facet at time $t=0$), $S(0,t)=S(L,t)=0$ for every t (i.e., the boundaries sides of the facet are absorbent). The solution of Eq. (A1) is

$$S(x,t)=\sum_{n=0}^{+\infty}\frac{4}{(2n+1)\pi}\sin\left(\frac{(2n+1)\pi x}{L}\right)e^{-[D\pi^2(2n+1)^2 t]/L^2}. \tag{A2}$$

To take into account the appearance of particles on the facet, we assume the process to be Poissonian so that the probability to have a particle appearing at time t is $(1/\tau)e^{-t/\tau}$. Thus the probability P that two particles are on the facet is

$$P=\int_0^\infty 1/\tau e^{-\frac{t}{\tau}}S(x,t)dt. \tag{A3}$$

To take into account that particles can appear on the facet on both ends, we take $\tau=\tau_3/2$, which holds at low temperatures. This leads to the expression

$$P=\frac{4\delta^2}{\pi}\sum_{n=0}^{+\infty}\frac{1}{2n+1}\frac{\sin[(2n+1)\chi]}{\delta^2+(2n+1)^2}, \tag{A4}$$

where

$$\delta^2=\frac{2L^2}{D\pi^2\tau_3}, \tag{A5}$$

$$\chi=\frac{\pi x}{L}. \tag{A6}$$

Using the formula[13]

$$\zeta(\delta,\chi)=\sum_{k=1}^{+\infty}\frac{\cos(k\chi)}{\delta^2+k^2}=\frac{\pi}{2\delta}\frac{\cosh[\delta(\pi-\chi)]}{\sinh(\delta\pi)}-\frac{1}{2\delta^2} \tag{A7}$$

we have

$$\sum_{n=0}^{+\infty}\frac{1}{2n+1}\frac{\sin[(2n+1)\chi]}{\delta^2+(2n+1)^2}=\int_0^{\chi}\left[\zeta(\delta,\chi')-\frac{1}{4}\zeta(\delta/4,2\chi')\right]d\chi'. \tag{A8}$$

So that, using Eqs. (A5) and (A6), we finally find the following expression for P:

$$P=1-\left[\frac{2\sinh[2\sqrt{\rho}(L-1)]}{\sinh[2\sqrt{\rho}L]}-\frac{\sinh(2\sqrt{\rho}(L/2-1))}{\sinh(2\sqrt{\rho}L/2)}\right], \tag{A9}$$

where $\rho=\tau_2/\tau_3$, and we have taken $x=1$ (the initial particle on the face is at position 1 at time $t=0$). We can expand expression Eq. (A9) for small ρ keeping the first term

$$P=2\rho(L-1)+o(\rho). \tag{A10}$$

APPENDIX B: PROBABILITY THAT TWO PARTICLES STICK ON THE FACE

In this part we evaluate the probability $P_\triangle$ that two particles stick on a facet with absorbing boundaries, knowing that at time $t=0$, one particle is on one end of the facet, and the other is at a position x_0 on the face. This problem can be mapped to a 2D problem in which, at time t, the first particle is at position y, and the second particle is at position x. This virtual particle moves diffusively in a square of side L; starting from position (x_0,a) (a is the lattice spacing). The quantity we are looking for is the probability for this virtual particle to reach the diagonal $y=x$ of the square. Thus we can consider the motion of the virtual particle in the triangle $0\leqslant x\leqslant y\leqslant L$. We call $D(x,y)$ the probability that a virtual particle starting at time $t=0$ from (x,y) leaves the triangle by the diagonal, $V(x,y)$, the probability that this particle leaves the triangle by its vertical side, and $H(x,y)$ the probability that this particle leaves the triangle by its horizontal side. We use here a continuous description: the discrete problem being far too difficult. It can be easily seen that D, V, and H satisfy Laplacian equations

$$\Delta D(x,y)=0, \quad \Delta V(x,y)=0, \quad \Delta H(x,y)=0 \tag{B1}$$

with the conditions

$$D(x,x)=1, \quad D(x,0)=0, \quad D(0,y)=0, \tag{B2}$$

$$V(x,x)=0, \quad V(x,0)=0, \quad V(L,y)=1, \tag{B3}$$

$$H(x,x)=0, \quad H(x,0)=1, \quad H(0,y)=0 \tag{B4}$$

$$\text{for} \quad \forall x \in [0,L] \quad \text{and} \quad \forall y \in [0,L],$$

and, moreover, we should have

$$D(x,y)+V(x,y)+H(x,y)=1, \tag{B5}$$

which states that the particle is sure to leave the triangle since all sides are absorbent. Instead of calculating directly $D(x,y)$, we will calculate $V(x,y)$ and $H(x,y)$.

We first calculate $V_{\Box}(x,y)$ and $H_{\Box}(x,y)$ which are the probability that one Brownian particle in a square with absorbing sides, respectively, leaves the square by the vertical side $x=L$ and by the horizontal side $y=0$. So we have

$$\Delta V_{\Box}(x,y)=0, \quad \Delta H_{\Box}(x,y)=0 \tag{B6}$$

with boundary conditions

$$V_{\Box}(x,L)=0, \quad V_{\Box}(x,0)=0, \tag{B7}$$

$$V_{\Box}(0,y)=0, \quad V_{\Box}(L,y)=1, \tag{B8}$$

$$H_{\Box}(L,y)=0, \quad H_{\Box}(0,y)=0, \tag{B9}$$

$$H_{\Box}(x,0)=1, \quad H_{\Box}(x,L)=0 \tag{B10}$$

$$\text{for} \quad \forall x \in [0,L] \quad \text{and} \quad \forall y \in [0,L].$$

The solution of Eq. (B6) with these conditions is

$$H_{\Box}(x,y)=\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{\sin\frac{(2m+1)\pi x}{L}}{2m+1}\,\frac{\sinh\frac{(2m+1)\pi(L-y)}{L}}{\sinh(2m+1)\pi}, \tag{B11}$$

$$V_{\Box}(x,y)=\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{\sin\frac{(2m+1)\pi y}{L}}{2m+1}\,\frac{\sinh\frac{(2m+1)\pi x}{L}}{\sinh(2m+1)\pi}. \tag{B12}$$

One now can deduce the values of $V(x,y)$ and $H(x,y)$ of our initial problem with a superposition of solutions to impose the condition $V(x,x)=0$ and $H(x,x)=0$:

$$V(x,y)=V_{\Box}(x,y)-V_{\Box}(y,x), \tag{B13}$$

$$H(x,y)=H_{\Box}(x,y)-H_{\Box}(y,x). \tag{B14}$$

Using Eqs. (B5), (B13), (B14), (B11), and (B12), we finally find an expression for $D(x_0,a)$:

$$D(x_0,a)=1-\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{\sin\frac{(2m+1)\pi a}{L}}{2m+1}\left[\frac{\sinh\frac{(2m+1)\pi x_0}{L}-\sinh\frac{(2m+1)\pi(L-x_0)}{L}}{\sinh(2m+1)\pi}\right]$$
$$-\frac{4}{\pi}\sum_{m=0}^{\infty}\frac{\sin\frac{(2m+1)\pi x_0}{L}}{2m+1}\left[\frac{\sinh\frac{(2m+1)\pi(L-a)}{L}-\sinh\frac{(2m+1)\pi a}{L}}{\sinh(2m+1)\pi}\right].$$

We now have to calculate the probability that the second particle is at position x_0 when the other one appears on the facet. We denote this probability $P(x_0)$. Then the probability we are looking for is simply

$$P_{\triangle}=\int_0^L D(x_0,a)P(x_0)dx_0. \tag{B15}$$

We are actually able to calculate the exact probability $P(x_0)$, but then we are not able to find a simple expression for $P_{\triangle}$, so we prefer to make the following approximation: In the limit of small temperature, the typical time needed for a particle to appear on the facet is about τ_3, which is long compared to the typical time a particle lasts on the facet (about $L\tau_2$ for a particle that starts near the edge). Thus, to a good approximation, the probability $P(x_0)$ has reached its stationary value. Taking into account only the first term of the series, we have

$$P(x_0)=\frac{\pi}{2L}\sin\frac{\pi x_0}{L}. \tag{B16}$$

With this expression Eq. (B15) becomes easy to calculate and we find

$$P_{\triangle}=1-\frac{\sinh\frac{\pi(L-a)}{L}-\sinh\frac{\pi a}{L}}{\sinh\pi} \tag{B17}$$

$$=\left(\frac{\cosh\pi+1}{\sinh\pi}\right)\frac{\pi a}{L}-\frac{\pi^2a^2}{2L^2}+o(1/L^2). \tag{B18}$$

So that we find that the leading term of $P_{\triangle}$ is proportional to $1/L$. We write this as

$$P_{\triangle}=\lambda\frac{1}{L}+o(1/L^2) \tag{B19}$$

$$\text{with}\ \ \lambda=\left(\frac{\cosh\pi+1}{\sinh\pi}\right)\pi. \tag{B20}$$

APPENDIX C: CALCULATION OF THE TIME TO LEAVE STATE 2

We calculate in this part the average time $\langle\tau\rangle$ for two particles on the facet either to bond, or either one of them to reach the boundary. This time corresponds to the time the system stays in state 2 in the Markov chain. Using the description of Appendix B with the virtual particle in the triangle, we are looking for the average time this particle needs to leave the triangle.

Let us call $S(x_0,y_0,t)$ the survival probability: i.e., the probability a particle starting at (x_0,y_0) at time $t=0$ is still in the triangle at time t. The average time $\langle\tau(x_0,y_0)\rangle$ the particle stays in the triangle is given by

$$\langle\tau(x_0,y_0)\rangle=\int_0^{\infty}S(x_0,y_0,t)dt. \tag{C1}$$

Moreover, calling $P_{\triangle}(x,y,x_0,y_0,t)$ the probability that one particle starting at (x_0,y_0) at time $t=0$ is at position (x,y) at time t, we have

$$S(x_0,y_0,t)=\int\int_{\triangle}P_{\triangle}(x,y,x_0,y_0,t)dxdy. \tag{C2}$$

Finally, we are only interested in $\langle\tau(x_0,1)\rangle$ since we know that our virtual particle starts at (x_0,a), so we have to average the time $\langle\tau(x_0,1)\rangle$ over all values x_0. To do this we use the approximate distribution given in Eq. (B16):

$$\langle\tau\rangle=\int_0^{L}P(x_0)\langle\tau(x_0,1)\rangle dx_0. \tag{C3}$$

So finally, using Eqs. (C1)–(C3), we need to evaluate

$$\langle\tau\rangle=\int_0^{L}\int_0^{\infty}\int\int_{\triangle}P(x_0)P_{\triangle}(x,y,x_0,1,t)dxdy\ \ dt\ \ dx_0. \tag{C4}$$

We now have to calculate $P_{\triangle}(x,y,x_0,1,t)$. As before, we find the solution in a square, and then by superposition, we deduce the solution in the triangle:

$$P_{\triangle}(x,y,x_0,1,t)=P_{\square}(x,y,x_0,1,t)-P_{\square}(x,y,1,x_0,t), \tag{C5}$$

$$P_{\square}(x,y,x_0,1,t)=\frac{4}{L^2}\sum_{m,n=1}^{\infty}\sin\frac{m\pi x_0}{L}\sin\frac{n\pi}{L}\times\sin\frac{m\pi x}{L}\sin\frac{n\pi y}{L}e^{-[D(m^2+n^2)\pi^2t]/L^2}. \tag{C6}$$

We find $\langle\tau\rangle$ integrating Eq. (C4) using Eqs. (C5) and (C6) over x_0 first, and then over x and y, and finally over t, we find

$$\langle\tau\rangle=\frac{L^2}{D\pi^3}\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \sin\frac{2k\pi}{L}\ \left[\frac{2}{k}-\frac{1}{k(2k+1)}\right]. \tag{C7}$$

We are interested in the leading term as $L\to\infty$, so let us define a function $f(u)$ by

$$f(u)=\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \sin(ku)\ \left[\frac{2}{k}-\frac{1}{k(2k+1)}\right]. \tag{C8}$$

$f(u)$ is a normally convergent series, so that

$$\frac{df(u)}{du}=\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \cos(ku)\ \left[2-\frac{1}{(2k+1)}\right] \tag{C9}$$

$$\overset{u\to0}{\mapsto}\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \left[2-\frac{1}{(2k+1)}\right] \tag{C10}$$

which is also convergent. The second term of the development is of order u^2 or smaller, so that integrating Eq. (C10), and using it in Eq. (C7), we find

$$\langle\tau\rangle=\frac{2L}{D\pi^2}\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \left[2-\frac{1}{(2k+1)}\right]+O(1/L). \tag{C11}$$

Thus $\langle\tau\rangle$ is proportional to L, and we write

$$\langle\tau\rangle=\kappa L\tau_2+O(1/L) \tag{C12}$$

$$\text{with}\ \ \kappa=\frac{4}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{1+4k^2}\ \left[2-\frac{1}{(2k+1)}\right]. \tag{C13}$$

APPENDIX D: CALCULATION OF THE TIME A PARTICLE NEEDS TO GO TO CENTER OF THE FACET

We now calculate the average real time $t_{p,q,\alpha}$ to go from state i to state $i+1$ assuming the average distance between the kinks or corners from which particles are emitted and the germ is $L/2$. This again can be posed as a Markov chain where

- state 0: no particle is on the facet;
- state 1: one particle coming from a kink is in position 1 on the facet;
- state 2: the particle is at position 2;

. . .

- state k: the particle is at position k; and state $L/2$ is absorbent.

Again we use τ_2 as the unit time. Using the same definition for the quantities p_i, q_i, and α_i as in the main text, we have

$$p_i=1/2, \tag{D1}$$

$$\alpha_i=0, \tag{D2}$$

$$q_i=1/2, \tag{D3}$$

$$\text{with}\quad i\geqslant1.$$

To calculate p_0 and α_0 we know that the real time an atom needs to leave a kink is τ_3, and as there are two kinks at the ends of the facet, $\tau_3/2$ is, to a good approximation, the average time to leave state 0. Thus that we find

$$p_0 = 2\rho, \tag{D4}$$

$$\alpha_0 = 1 - 2\rho. \tag{D5}$$

Calling n_i the average time to go from state i to the absorbent state $L/2$, we have the equations

$$n_0 = 1 + \alpha_0 n_0 + p_0 n_1, \tag{D6}$$

$$n_k = 1 + \frac{n_{k-1}}{2} + \frac{n_{k+1}}{2}, \tag{D7}$$

$$\text{with} \quad k \geqslant 1,$$

$$n_{L/2} = 0, \tag{D8}$$

and $n_{L/2} = 0$. Summing Eqs. (D7) from $k = 1$ to j, and then from $j = 1$ to $L/2 - 1$, and using Eq. (D8), one finds

$$n_1 = \frac{L-2}{L} n_0 + \frac{L-2}{2}, \tag{D9}$$

and Eq. (D6) permits to obtain n_0

$$n_0 = \frac{L}{2p_0} + \frac{L(L-2)}{4}. \tag{D10}$$

Going back to real time, one finds the average time τ a particle needs to leave a kink and reach the center of the facet is

$$t_{p,q,\alpha} = \frac{L}{4}\tau_3 + \frac{L(L-2)}{4}\tau_2. \tag{D11}$$

APPENDIX E: CALCULATION OF n_0

To carry out the calculation, we can first calculate the n_k for $k \geqslant 1$. Noting that $p = q$, we have from Eq. (28)

$$(n_{k+1} - n_k) = (n_k - n_{k-1}) - 1/p, \tag{E1}$$

so that summing from $k = 4$ to j, and then from $j = 4$ to l, and using $n_{l+1} = 0$, we find

$$(l-1)n_3 = (l-2)n_2 + 1/p\left(\frac{(l-2)(l-1)}{2}\right). \tag{E2}$$

Inserting this result in Eq. (27) we find n_2 as a function of n_1, in the same way, using Eq. (26), one can deduce the equation for n_1:

$$n_1(1 - \alpha_1 - p_1 B) = 1 + p_1 A + q_1 n_0, \tag{E3}$$

where

$$A = \frac{1 + \dfrac{p_2}{p}\dfrac{l-2}{2}}{1 - \alpha_2 - p_2\dfrac{l-2}{l-1}}, \tag{E4}$$

$$B = \frac{q_2}{1 - \alpha_2 - p_2\dfrac{l-2}{l-1}}. \tag{E5}$$

(E6)

We now calculate the case $k<0$. Calling $m_j = n_{-j}$ for every j, and summing Eq. (21) from j to $z-1$, one finds

$$m_z - m_{z-1} = m_j - m_{j-1} - \frac{z-j}{p^*}, \tag{E7}$$

and Eq. (20) yields $m_l - m_{l-1} = 1/2p^*$. Using this in Eq. (E7) and taking $j = 3$, one finds

$$m_3 - m_2 = \frac{l-3}{p^*} + \frac{1}{2p^*}. \tag{E8}$$

Using Eqs. (23) and (24), one finds

$$n_{-1} = \frac{1}{q_1^*} + \frac{p_1^*}{q_1^* q_2^*} + \frac{p_1^* p_2^*}{q_1^* q_2^* p^*}(l - 5/2) + n_0. \tag{E9}$$

One can know obtain the value of n_0 from Eqs. (E3), (E9), and (25):

$$p_0\left(1 - \frac{q_1}{1 - \alpha_1 - p_1 B}\right)n_0 = 1 + p_0\frac{1 + p_1 A}{1 - \alpha_1 - p_1 B} + q_0\left(\frac{1}{q_1^*} + \frac{p_1^*}{q_1^* q_2^*} + \frac{p_1^* p_2^*}{q_1^* q_2^* p^*}(l - 5/2)\right). \tag{E10}$$

Then, using Eqs. (8)–(19) we can calculate A and B:

$$A = \frac{L}{4\rho}\frac{(l-1)(l-2)}{\left(\dfrac{L}{\lambda} - 1\right)(l-1) + 1} + \frac{\dfrac{\kappa}{\lambda}L^2(l-1) + \dfrac{L(L-2)(l-2)(l-1)}{4}}{\left(\dfrac{L}{\lambda} - 1\right)(l-1) + 1} + o(1),$$

$$B = 1 - \frac{1}{\left(\dfrac{L}{\lambda} - 1\right)(l-1) + 1}.$$

And finally, the expression of n_0 is

$$n_0=\frac{1}{\rho^2}\frac{(L+2l)}{4L(L-1)}\left[\left(\frac{L}{\lambda}-1\right)(l-1)+1\right]+O(1/\rho). \tag{E11}$$

We report here only the leading term: the expressions of the quantities p_i, q_i, and α_i permit us to calculate n_0 up to order 1, but these terms are truly ugly and it does not seem relevant to give them here.

Going back to real time, we find that the time $\tau(L,l)$ to nucleate a new row on a facet is given by

$$\tau(L,l)=\frac{\tau_3^2}{\tau_2}\frac{(L+2l)}{4L(L-1)}\left[\left(\frac{L}{\lambda}-1\right)(l-1)+1\right]+O(\tau_3). \tag{E12}$$

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[7] This formulation of the relaxation time as a function of N/N_c permits us to resolve the apparent paradox mentioned in Ref. 5. Namely, that extrapolating the low-temperatures regime to higher temperatures, one could infer that large islands would relax faster at high temperature than at low temperature. The curve $\log(t_{relaxation})$ as a function of $\log(N)$ at a given temperature T_1 is obtained by translation of the curve at temperature T_0 by a vector $N_c(T_1)/N_c(T_0)(^1_5)$. Since the slope of this translation is greater than the slopes of $\log(t_{relaxation})$ as a function of $\log(N)$, thus two curves at different temperatures can not cross each other.

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