

Reabsorption effect and spatial ordering in island ripening

D. M. Tarr and P. A. Mulheran

Department of Physics, University of Reading, Whiteknights, P.O. Box 220, Reading RG6 6AF, United Kingdom

(Received 25 November 2002; published 11 August 2003)

A model for detachment-limited island ripening is analyzed in terms of a reabsorption (or pedophagous) effect where islands releasing monomers can reabsorb their own offspring. When the effect is artificially turned off, ripened island arrays are spatially disordered and the island growth rates and size distribution are easily understood in terms of a classic mean field theory. With the pedophagous effect included, the arrays develop a spatial ordering consistent with experimental studies. The ordering is quantified through a correlation between island size and the number of nearby neighbors, yielding modified mean field island growth rates and a much-improved expression for the island size distribution. It is suggested that the spatial ordering and our explanation are widely applicable to ripening systems.

DOI: 10.1103/PhysRevE.68.020602

PACS number(s): 81.15.Aa, 81.10.Aj, 68.55.Ac

Nanostructure evolution and its scaling properties are topics of great interest, motivated by the obvious technological advances made in this field. Much work has focused on the growth and ripening of two-dimensional island structures (see the review by Zinke-Allmang [1]) due to its relevance to crystalline systems [2]. It has recently been realized that the ripening of islands leads to spatial as well as size ordering [3], where the island arrays self-organize into a scale-invariant state that does not depend sensitively on the initial island distribution. Why this phenomenon occurs is a basic yet challenging question for statistical physics of nonequilibrium systems.

Most theoretical work on island ripening has concerned the case of diffusion-limited growth [4–7]. However, for many systems of interest to nanotechnology the ripening is limited by the interfacial kinetics of monomer attachment/detachment at the island edges [8–10]. Once free from its parent, a monomer rapidly diffuses to be reabsorbed by another (or the parent) island. In this paper we study a Monte Carlo simulation of island ripening limited by monomer detachment rates. We find that the system evolves to a scaling state where the spatial ordering is comparable to that discovered by Carlow and Zinke-Allmang [3]. We show that this ordering is an unexpected consequence of the pedophagous effect, where parent islands reabsorb their own offspring monomers. We also quantify the spatial ordering through an intuitive correlation between an island's size and its number of first-shell neighbors. This correlation then leads us to an improved understanding of the scaling island size distribution that evolves in the system.

In their study of two-dimensional island ripening on Si(001) Bartelt, Theis, and Tromp derived the island size distribution from a straightforward mean field theory where an island captures monomers at a rate proportional to its diameter [9]. This model is in fact the same as that solved by Hillert for grain growth in two dimensions [11], based on the classic Lifshitz-Slyozov theory for Ostwald ripening [12]. Bartelt, Theis, and Tromp's limited island size data seem to follow the Hillert distribution reasonably well, although there is evidence that the experimental data do not conform to the theoretical large-size cutoff and peak position. In our simulations it is found that the island size distribution devi-

ates unequivocally from the Hillert theory in the same manner. The cause of this is the aforementioned spatial ordering and its correlation with island size. Utilizing the correlation leads us to an improved geometric mean field theory that yields a better prediction for the scaling island size distribution.

In our Monte Carlo simulations we study the ripening of immobile circular two-dimensional islands using a square mesh to represent the substrate. On each step of the simulation, one monomer is released from a randomly chosen island and diffused upon the lattice until it impinges upon any island, whereupon it is absorbed. Island sizes and their footprints on the mesh are updated accordingly by assuming that the islands keep perfect circular shape, so that edge-atom mobility is fast on the scale of monomer release. In this way the simulation models detachment-limited ripening where the emission rate is independent of island size, so that the average area grows linearly in time [8,9]. As discussed below, we do not believe that this simple choice of model profoundly affects the conclusions we reach.

Typical results of the Monte Carlo simulation are shown in Fig. 1(a), where the islands have been ripened until the number density is reduced by an order of magnitude. By this stage the simulation has reached the scale-invariant state, where statistical properties such as the distribution of island sizes measured relative to the mean do not change over time. It is immediately apparent that the island array has developed a degree of spatial order. This spatial order is quantified in terms of first and second nearest-neighbor separation distributions in Fig. 2, for direct comparisons with the empirical fits used by Carlow and Zinke-Allmang to characterize their experimental results [3]. The agreement for first nearest-neighbor separations is good, and the deviation in the second nearest-neighbor separations is similar to that in the original data of Carlow and Zinke-Allmang [3]. This suggests that the spatial ordering is a ubiquitous phenomenon of ripening that is not sensitive to the atomistic details of the system. Indeed, modifying the simulation to make the monomer release rate size dependent (specifically, proportional to island size or its square root) produces the same spatial order. In addition, it is also easy to test whether the spatial ordering depends on the starting configuration of the islands. The simulation shown in

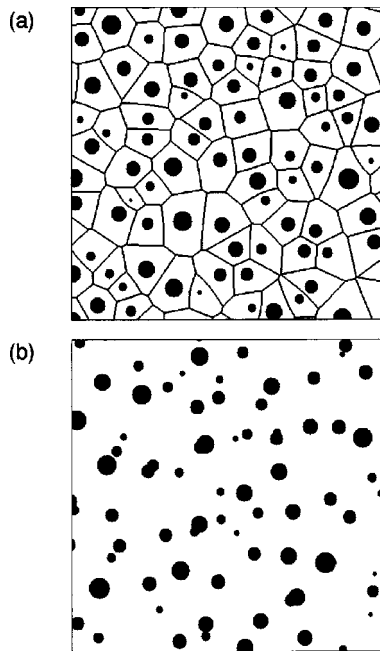


FIG. 1. Snapshots of ripened islands for (a) normal PE simulation and (b) NPE simulation of island ripening. Substrate coverage is 10% in both cases. In (a) a Voronoi-type network for the island edges has been superposed.

Fig. 1(a) started with islands formed in a simulation of island nucleation and growth during vapor deposition [13]. We have also run the simulation starting with perfect order, i.e., regular arrays of equisized islands; with randomly positioned and randomly sized islands; and from different substrate cover-

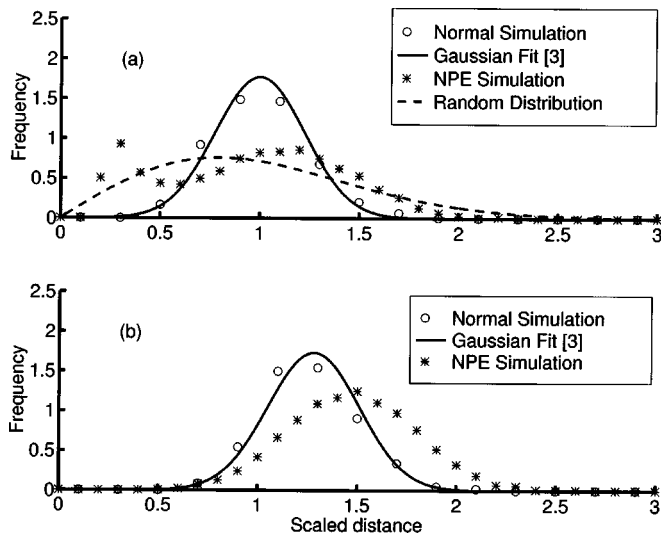


FIG. 2. (a) First and (b) second nearest-neighbor separation distributions from the normal PE and NPE simulations, compared to the empirical Gaussian fits to experimental data of Carlow and Zinke-Allmang [3]. In (a) the distribution for a random scattering of points in a plane is shown for comparison. Thirty runs have been used to get the simulation data in this and the following figures, each starting with 3000 islands on a 1000×1000 lattice at 10% substrate coverage and ripened until 300 islands remain.

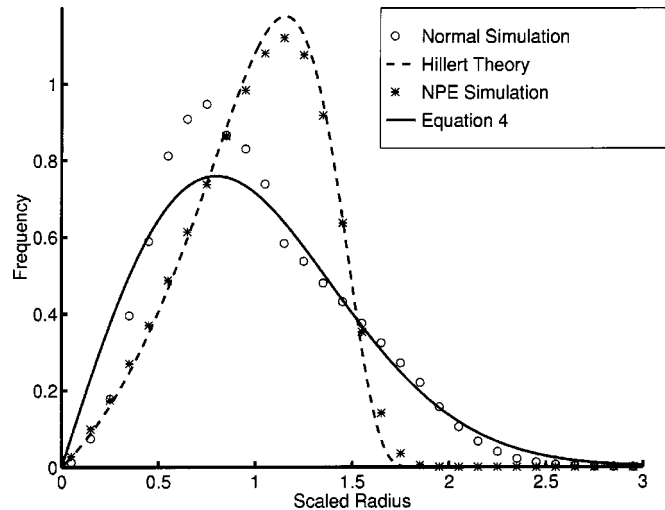


FIG. 3. Scaled island size distributions for normal PE and NPE simulations compared to theoretical models discussed in the text.

age. We always find that the island arrays evolve to the same scale-invariant statistically self-similar state.

How does the spatial order arise? Consider the early stages of a simulation with randomness in both island size and position. The immediate environment of an island is independent of its size, and is surrounded by other, monomer-emitting islands in a mean field manner. Growth should then proceed as described by the Hillert model where the average growth rate of islands with the same radius is proportional to that radius [9,11] (see below). However the island size distribution that evolves in the simulations clearly disagrees with the Hillert model as shown in Fig. 3. Thus the environment of the ripened islands does depend on size; the environment is perturbed over time by the very presence of the island itself.

This idea is easily tested using a modified simulation where the pedophagous effect is artificially switched off. An island is now allowed to absorb monomers from neighbors, but it cannot absorb its own offspring. In this way islands are preserved in an approximately size-independent environment. Results of this modified, nonpedophagous effect (NPE) simulation are shown in Fig. 1(b). Starting from the same configuration as in Fig. 1(a), we see that the ripened islands display little or no spatial ordering. As a consequence, many of the islands overlap, although they are still considered as separate islands (i.e., no coalescence occurs in this *artificial* model) for clarity in the following discussion. The absence of pronounced spatial order is confirmed in the nearest-neighbor separation distributions shown in Fig. 2.

The origins of the spatial ordering can now be understood. In Fig. 2(a) the modified NPE simulation has a small-scaled size peak, and in consequence the main peak of the distribution is shifted to larger scaled size. The small-size peak shows how very near neighbors are extremely stable, with one island feeding off the other regardless of size, and this feature is also present in NPE simulations with the size-dependent monomer release rates mentioned above. However, in the normal pedophagous effect (PE) simulation the larger island of a closely spaced pair will grow at the ex-

pense of the smaller. This is because the islands are in competition with one another for all monomers including their own offspring, and the larger island shadows the smaller much more effectively. This shadowing is removed when the pedophagous effect is switched off, proving that in the normal PE simulation spatial order develops through the rapid local ripening of closely spaced pairs. This mechanism has been conjectured in the literature before [4,14], and direct local ripening is the basis for understanding the detailed evolution of individual islands in both interface and diffusion limited ripening [8,15]. However, the NPE simulation shows unequivocally the key role that local effects play in the establishment of *overall* spatial ordering.

Given its spatial disorder, it is to be expected that the Hillert model will accurately describe the island size distribution that evolves in the NPE simulations. In Bartelt, Theis, and Tromp's approach [9] that yields the Hillert model, islands evolve through emitting at a constant rate and capturing monomers in proportion to their scaled radius, so that islands larger than the mean size grow and those smaller shrink:

$$\frac{ds}{dt} = \left(\frac{r}{\bar{r}(t)} - 1 \right). \quad (1)$$

Here time t is scaled by the monomer release rate, r is island radius, $\bar{r}(t)$ is its average that grows as $t^{1/2}$, and $s = \pi r^2$ is the island size. The solution of the continuity equation with the growth rate equation (1) yields the scaling island size distribution [11]

$$f(u) = \begin{cases} \frac{u}{2} \left(\frac{2}{2-u} \right)^4 \exp\left(\frac{-2u}{2-u} \right), & u < 2 \\ 0, & u \geq 2, \end{cases} \quad (2)$$

where $u = r/\bar{r}$ is the scaled island radius. Equation (2) is displayed alongside the size distribution measured in the NPE simulations in Fig. 3 and extremely good agreement is observed. In contrast, the island size distribution from the normal PE simulation clearly violates the cutoff at $u=2$ and is peaked at a lower scaled size [9].

The failure of the Hillert model to provide an adequate description of the normal PE simulation's island size distribution implies a size-dependent dimension to its spatial order [16]. Large islands grow more rapidly than the Hillert model suggests because they tend to have more nearby (or first-shell) neighbors than smaller islands, and therefore are exposed to more monomer emitters than the smaller ones. We can approximate the number of first-shell neighbors using a Voronoi-type construction as shown in Fig. 1(a). The Voronoi-type edge cell for each island is the region of substrate closer to that island's edge than to any other absorbing edge in the island array [13]. The number of first-shell neighbors is the same as the number of sides on the edge cell. Since, in this model, islands grow at the expense of their neighbors (monomers are very unlikely to diffuse past first-shell neighbors to more distant absorbers), the local density of material remains constant. This implies that the area of the edge cell associated with an island is proportional to its size,

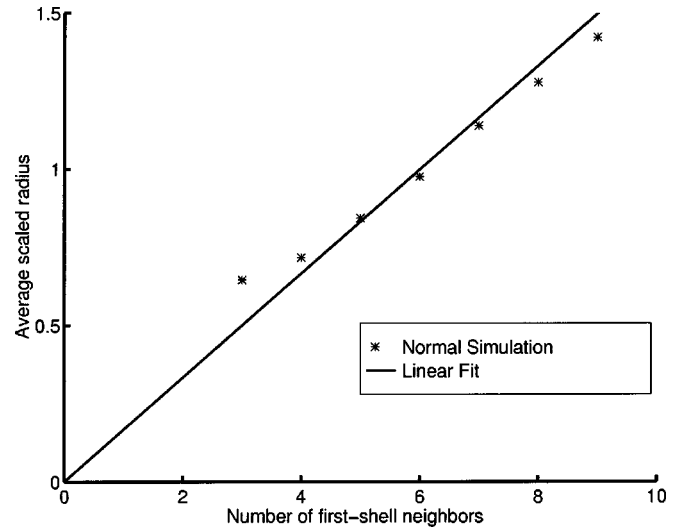


FIG. 4. Correlation between averaged island size and edge-cell shape in the normal PE simulation. Standard errors are equal to or less than the size of the symbols.

and that the number of first-shell neighbors is proportional to island radius. This correlation is tested in Fig. 4, and it is apparent that a strong relationship of the type predicted exists.

This correlation can be used to improve upon the Hillert model for normal PE island ripening. As shown above, in the random spatial environment of the NPE simulation, islands grow and shrink according to Eq. (1). This is confirmed in Fig. 5(a) demonstrating that the basic premise that islands capture diffusing monomers in proportion to their diameters is correct. The growth law for normal PE ripening can now be modified in light of the above. Since the number of first-

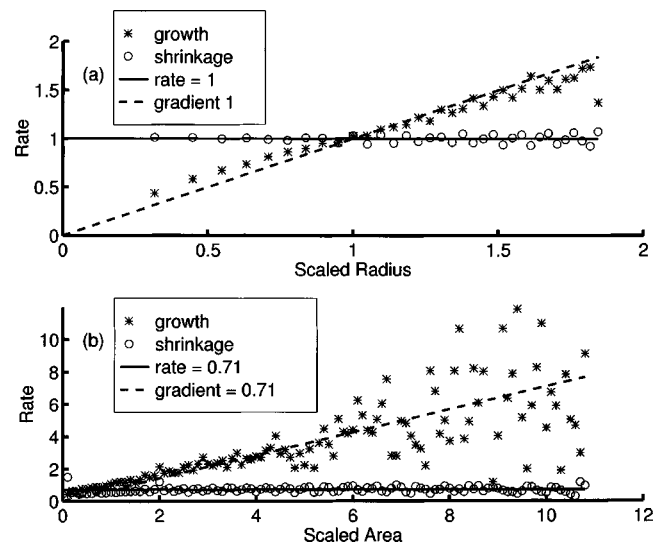


FIG. 5. Growth and shrink rates for (a) NPE simulation and (b) normal PE simulation as a function of scaled island radius and area, respectively. Data are acquired by monitoring monomer histories while freezing island sizes at the end of the simulations. In (a) the rates are compared to those of the Hillert model. In (b) the average monomer release rate (0.71) is the average of the data points shown, and the growth rate data fit well to the gradient 0.71 as in Eq. (3).

shell donors is proportional to radius, in combination with the capture cross-section rule we have

$$\frac{ds}{dt} = c \left(\frac{r^2}{\bar{r}^2} - 1 \right) = c \left(\frac{s}{\bar{s}} - 1 \right). \quad (3)$$

Here c is the corrected emitter rate that allows for monomer reabsorption by the parent island (the pedophagous effect). We assume that c is size independent; mean field arguments reveal only a slow dependence of the monomer escape probability on island radius. The growth and shrink rates for the normal PE simulation are shown in Fig. 5(b), and compare well to the form suggested in Eq. (3) with $c=0.71$, implying that on average 71% of monomers released actually escape from their parents. This model has the very simple solution $\exp(-s/\bar{s})$ for the scaled island size distribution. In terms of the scaled island radius u , it is

$$g(u) = \frac{\pi}{2} u \exp\left(-\frac{\pi}{4} u^2\right). \quad (4)$$

Equation (4) is compared to the normal PE simulation data in Fig. 3 and reasonable agreement is found. The deviation between the data and Eq. (4) at small radius in Fig. 3 is due to the failure of Eq. (3) and its approximations at small

size. However, note that both Eq. (4) and the simulation data have a long large-size tail that clearly violates the Hillert model cutoff at $u=2$, and both have peak position at scaled radius $u \approx 0.8$. These features are also apparent in Bartelt and co-worker's experimental data [8,9].

In summary, we have investigated detachment-limited ripening of two-dimensional islands using Monte Carlo simulations. We have shown that the spatial order that emerges in the ripening island arrays is a ubiquitous phenomenon, and that it is a consequence of the pedophagous effect that ensures the dissolution of small islands that are close neighbors to large ones. The spatial ordering is destroyed upon switching off the pedophagous effect leading to an island size distribution described well by a simple geometric mean field theory that is the same as Hillert's model for two-dimensional grain growth. In the normal PE simulation the spatial order has a size-dependent dimension whereby large islands have more first-shell neighbors from whom they capture monomers. This leads to a simple, intuitive explanation of the island size distribution's deviation from the Hillert model. Finally we note that our explanation of spatial ordering and its impact on the island size distribution is quite distinct from recent work where strain effects are used to induce spatial or size ordering [17,18].

-
- [1] M. Zinke-Allmang, *Thin Solid Films* **346**, 1 (1999).
 [2] *Atomistic Aspects of Epitaxial Growth*, Vol. 65 of NATO Science Series II, edited by M. Kotrla, N. I. Papanicolaou, D. D. Vvedensky, and L. T. Wille (Kluwer Academic, London, 2002).
 [3] G. R. Carlow and M. Zinke-Allmang, *Phys. Rev. Lett.* **78**, 4601 (1998).
 [4] M. Marder, *Phys. Rev. A* **36**, 858 (1987).
 [5] T. M. Rogers and R. C. Desai, *Phys. Rev. B* **39**, 11 956 (1989).
 [6] A. J. Ardell, *Phys. Rev. B* **41**, 2554 (1990).
 [7] J. A. Marqusee, *J. Chem. Phys.* **81**, 976 (1984).
 [8] W. Theis, N. C. Bartelt, and R. M. Tromp, *Phys. Rev. Lett.* **75**, 3328 (1995).
 [9] N. C. Bartelt, W. Theis, and R. M. Tromp, *Phys. Rev. B* **54**, 11 741 (1996).
 [10] O. Cavalleri, A. Hirstein, and K. Kern, *Surf. Sci.* **340**, L960 (1995).
 [11] M. Hillert, *Acta Metall.* **13**, 227 (1965).
 [12] I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961).
 [13] P. A. Mulheran and J. A. Blackman, *Phys. Rev. B* **53**, 10 261 (1996).
 [14] J. P. Hirth, *J. Cryst. Growth* **17**, 63 (1972).
 [15] K. Morgenstern, G. Rosenfeld, and G. Comsa, *Surf. Sci.* **441**, 289 (1999).
 [16] G. R. Carlow, D. D. Perovic, and M. Zinke-Allmang, *Appl. Surf. Sci.* **130**, 704 (1998).
 [17] F. Liu, A. H. Li, and M. G. Lagally, *Phys. Rev. Lett.* **87**, 126103 (2001).
 [18] Z. Gai, B. Wu, J. P. Pierce, G. A. Farnan, D. Shu, M. Wang, Z. Zhang, and J. Shen, *Phys. Rev. Lett.* **89**, 235502 (2002).