PHYSICAL REVIEW B **69**, 121406(R) (2004)

Quasicontinuum Monte Carlo: A method for surface growth simulations

G. Russo
Dipartimento di Matematica ed Informatica, Università di Catania, 95125 Catania, Italy

L. M. Sander
Michigan Center for Theoretical Physics and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120, USA

P. Smereka
Michigan Center for Theoretical Physics and Department of Mathematics, University of Michigan, Ann Arbor, Michigan 48109-1120, USA

(Received 15 December 2003; published 17 March 2004)

We introduce an algorithm for treating growth on surfaces which combines important features of continuum methods (such as the level-set method) and kinetic Monte Carlo (KMC) simulations. We treat the motion of adatoms in continuum theory, but attach them to islands one atom at a time. The technique is borrowed from the dielectric breakdown model. Our method allows us to give a realistic account of fluctuations in island shape, which is lacking in deterministic continuum treatments and which is an important physical effect. Our method should be most important for problems close to equilibrium where KMC becomes impractically slow.

DOI: 10.1103/PhysRevB.69.121406 PACS number(s): 68.55.Jk, 68.35.Fx, 81.15.Aa

Epitaxial growth on surfaces is of central importance both for applications and as a very interesting example of statistical processes out of equilibrium.[1] We may idealize the process as the introduction of new atoms (adatoms) onto a crystal surface with flux F; the adatoms then diffuse, with diffusion coefficient D, nucleate islands or attach to existing islands. During the early stages of growth, the submonolayer case, the island size and shape distribution is a matter of substantial practical and theoretical interest.

The island growth process is commonly modeled by kinetic Monte Carlo (KMC) or continuum models. In KMC, internal noise processes are automatically represented within the model and each adatom is represented individually. Therefore, when there are many adatoms (e.g., close to equilibrium) such simulations slow down considerably. A deterministic continuum model which represents the adatoms as a continuous fluid does not have this problem, and should be much faster. There has been considerable work in the development of such models for epitaxial growth (see Refs. 2, 3 and references therein). In some cases they have been quite successful, but sometimes they do not reproduce experimental results. One reason for such problems is that deterministic continuum models neglect important fluctuations. In this paper we present a method of dealing with some fluctuations without giving up the advantages of a continuum treatment. We call this approach quasicontinuum Monte Carlo (QCMC). The most important use of this method will be in cases where fluctuations are important, but which would be difficult to treat with KMC because of the presence of a large number of adatoms. A computation in a similar spirit has been given in Refs. 4,5. However, the present approach differs in a number of important ways, which we will discuss below.

There are several sources of fluctuations in the growth process. The one we consider here is the fact that when atoms attach to islands they do so one at a time—that is, there is *shot noise* in the island growth process. This is important because island growth limited by diffusion is *intrinsically unstable*. The surface of the island will grow fingers due to the analog of the well-known Mullins-Sekerka instability of metallurgy.[6] In the context of thin film growth the instability was discussed in detail by Bales and Zangwill.[7] The reason for unstable growth is easy to see: if a finger on the edge of an island starts to grow it will project out onto the terrace and be fed by more adatoms than the portions behind. The finger will grow longer, and be fed by still more flux, etc. Edge diffusion and other restructuring processes smooth out the fingers, and the final shape depends on the competition between unstable growth and smoothing.

An extreme case of the diffusively unstable growth is represented by the diffusion-limited aggregation (DLA) model of Witten and Sander.[8] In this model all smoothing processes are neglected and growth takes place so slowly that one random walking adatom at a time is considered. DLA clusters are sprawling fractal objects with many branches which resemble some cases of island growth.[9,10] There is a variation of the model called the dielectric breakdown model (DBM)[11] in which random walkers are not used. Instead the Laplace equation is solved outside the aggregate for a field ρ which represents the probability density of walkers, and the growth algorithm is to add one particle at a time with probability proportional to $\partial\rho/\partial n$ at the surface. Thus the DLA limit can be successfully treated by a model in which the adatoms are a continuum. However, methods such as the level-set method[3] cannot go to this limit and thus cannot produce dendritic islands which are seen in experiment.

The unstable modes for the interface of the islands are present in level-set models, of course. However, the reason why the DBM limit is not achieved is that the growth process is represented by deterministically advancing a continuum interface according to the flux of the adatom fluid into the surface [see Eq. (4) below]. In this algorithm the amplitude of the perturbations to a smooth interface are not correctly represented: they are given either by the initial conditions or by computer roundoff errors. In the experiment, however, there is a mechanism for feeding the instability: each adatom

attaches not as a spread-out advance of the interface, but as an atom. In the case of DLA the result is that noise in the shape is present at all scales[12] and does not average out.

We should mention that there are other fluctuations which we will not treat. For example, there are density fluctuations in the adatom fluid which are important in the nucleation of new islands. There is a method[13] to treat this within level-set theory that we could employ. We will not consider such processes in this work, but rather look at the shape fluctuations of existing islands.

The QCMC algorithm goes as follows: we treat the islands on the surface as crystals containing discrete atoms which occupy the sites of a lattice. To illustrate the method we use a square lattice here. On the other hand, the adatoms are treated as a continuum whose surface density is ρ, and which is governed by

$$\partial_t \rho = D\nabla^2 \rho + F. \tag{1}$$

In practice we solve this equation numerically on a discrete square grid which is commensurate with the crystal.

Equation (1) is solved with periodic boundary conditions on the edge of the system. The important physics of growth is incorporated into the boundary condition at the surface of the island. We put for the net current of adatoms onto the edge of the island,

$$D\frac{\partial \rho}{\partial n} = \mp k_{\pm}(\rho - \rho_o). \tag{2}$$

Here k_- governs the attachment rate from the top of the island and k_+ from the terrace adjacent to the island. If k_- is small, we have an Ehrlich-Schwoebel barrier.

In the case of irreversible growth only the first term in brackets in Eq. (2) would be present, and the current is inward, leading to island growth. The other term ρ_o accounts for the detachment of atoms from the island and depends on the position on the island boundary. Physically, the boundary condition must allow for faster detachment at corners, say, than at flat surfaces. We represent this in a way that allows us to compare directly with the bond-counting version of KMC,

$$\rho_o = \exp(-nE/k_B T). \tag{3}$$

Here n is the number of nearest-neighbor bonds that must be broken to *completely detach* (see below) the atom in question and add it to the adatom sea. The value of n depends on the environment of the detaching atom. We imagine that atoms can break bonds by moving along lattice directions. Also, E is the bond energy and T is the temperature. Of course, we can easily incorporate bonding to more distant neighbors.

The interpretation of the number of bonds, n, is a bit delicate. In Fig. 1 we show some examples of what we mean by ''complete detachment.'' For our square lattice, to detach an atom on a [10] surface we need to break three bonds. However, for a [11] surface, in order to detach from the surface, an atom must first break two bonds, and then subsequently, one more—see Fig. 1. Thus, for a [11] surface we set $n=3$ as well because this corresponds to the product of the probabilities of the two processes. In effect, we have coarse-grained. For other possible surface environments it is not difficult to tabulate the correct value of n.

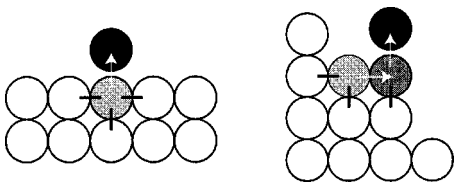

FIG. 1. (a) Detaching from a [10] surface can be done in one step, and breaks three bonds. (b) Fully detaching from a [11] surface in two steps also breaks three bonds.

In a pure continuum model, the velocity of the island growth would be determined by mass conservation,

$$v_n = a^2 D\left[\frac{\partial \rho}{\partial n}\right], \tag{4}$$

where a is the lattice constant and $[\cdot]$ denotes the jump across the island boundary. Note that we can interpret Eq. (2) in a way which is familiar in studies of crystal growth.[14] By combining Eqs. (2) and (4) we find an equation for the density at the surface,

$$\rho - \overline{\rho} = (\rho_o - \overline{\rho}) + \alpha v_n, \tag{5}$$

where $\alpha = 1/(a^2[k_+ + k_-])$ and $\overline{\rho}$ is the equilibrium density near a flat surface. That is, we are including both local equilibrium and kinetic terms in our boundary condition. The difference $\rho_o - \overline{\rho}$ is a measure of the number of dangling bonds on the surface, and thus of the curvature (upon coarse graining). The first term in Eq. (5) is related to the familiar Gibbs-Thompson boundary condition of crystal growth and the second is a kinetic term.

In QCMC we implement Eq. (4) in a way that *includes fluctuations*. Consider first a case where attachment is the only important process. Then we solve Eqs. (1) and (2) and compute the total flux onto the island boundary using Eqs. (2) and (4). When the total flux exceeds one atom then an adatom is attached to the boundary at random with the probability proportional to v_n (exactly as in the DBM model.) In the case where detachment is also present we consider the surface to be partitioned into the part where the net flux is inward (growth), and attach atoms with probability density $\propto v_n$, and outward (detachment) and remove island atoms with probability density $\propto -v_n$.

We have implemented QCMC and compared the results to a KMC code on the same square lattice using nearest-neighbor bonding. We use the hopping rate of an adatom to set the unit of time, and the lattice constant to be unity. We have two independent parameters namely D/F, and $\epsilon = E/k_B T$. We can also add edge diffusion, but here we have not done so. The KMC code is written using the method described in Ref. 15 which takes advantage of the fact that there are only a few independent jump probabilities for a bond-counting model. We find that, as expected, at large ϵ, the KMC code is much faster. However, for $\epsilon = 1.5$ and with about 300 adatoms in a 40×40 system the speeds are com-

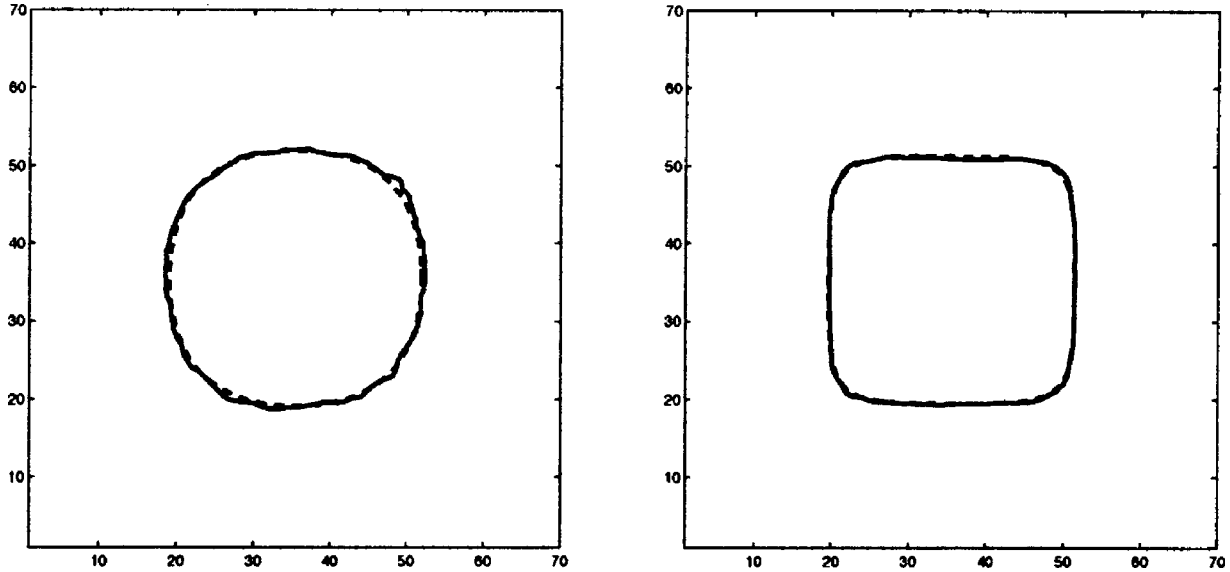

FIG. 2. QCMC simulations of the average profile of an equilibrium island compared with exact results. Left is for $\epsilon=2$ and right for $\epsilon=5$. The heavy line is from the simulation and the dotted line is the exact result. The agreement is excellent.

parable. In situations such as heteroepitaxy[16] there are a great many independent probabilities to jump and KMC is slower.

The procedure outlined above for choosing n, the number of bonds broken to fully detach from the interface, may seem arbitrary. However, we can justify it by its results. To this end, we show that QCMC gives the correct shape for an island in equilibrium with adatoms. This shape is known exactly[17] from a mapping to the 2d Ising model. We did simulations with $F=0$ starting with a square island, and ran our code for a long enough time that the system seemed to be in equilibrium. In Fig. 2 we show some results superimposed on the exact results for various temperatures. The simulation results are ensemble averages; that is, we did 20 independent simulations and averaged the density of the island after shifting the center of mass of each one to be at the origin. The dotted line in Fig. 2 is the contour line where the averaged island density is 1/2.

We now present some more results to demonstrate the technique. If growth dominates detachment we should have DLA-like structures. Whether this occurs depends on T and D/F.[18] For low temperature, Figs. 3 and 4, we see the transition in a very clear way. Figure 5 shows a higher T case. Of course, all of these effects can be seen in KMC simulations. In other simulations (not shown), we have demonstrated that edge diffusion also smoothes out dendritic shapes, as expected. The virtue of our method will be to treat systems near equilibrium where the dynamics of fluctuations are of interest and where there are many adatoms, as in Fig. 5.

Another example is the thermal broadening of steps due to repeated attachment and detachment of adatoms. The theoretical expectation[19,20] is that the thermal width w of a step should depend on the rate-limiting mechanism for step motion. In our model, without surface diffusion, this will be the either detachment from the step or diffusion on the terrace.

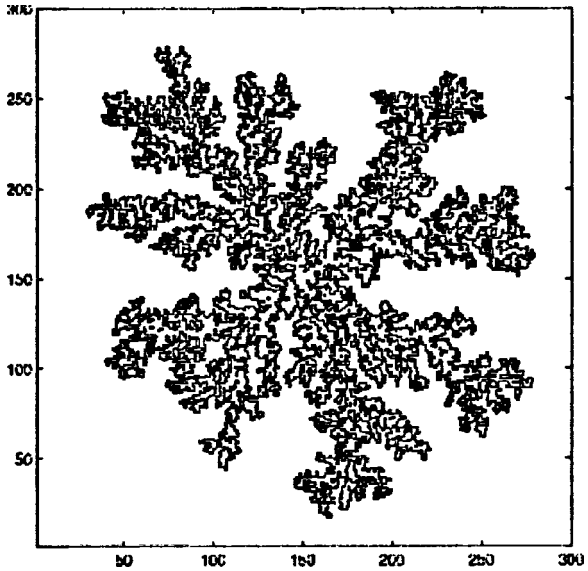

FIG. 3. Irreversible (low T) growth for $D/F=10^5$.

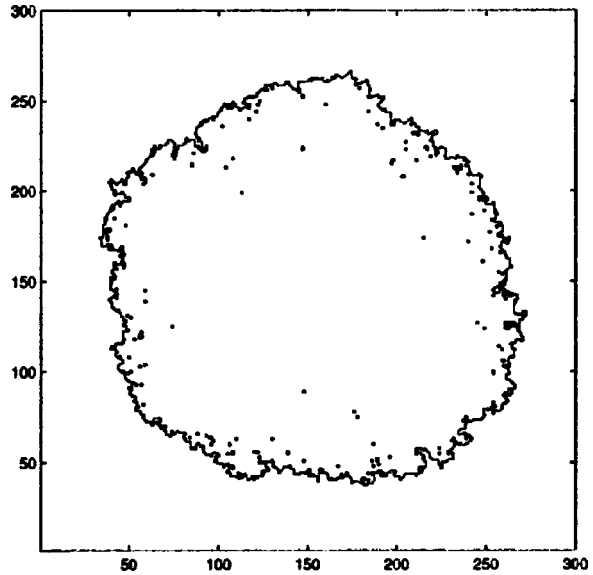

FIG. 4. Irreversible (low T) growth for $D/F=10^2$.

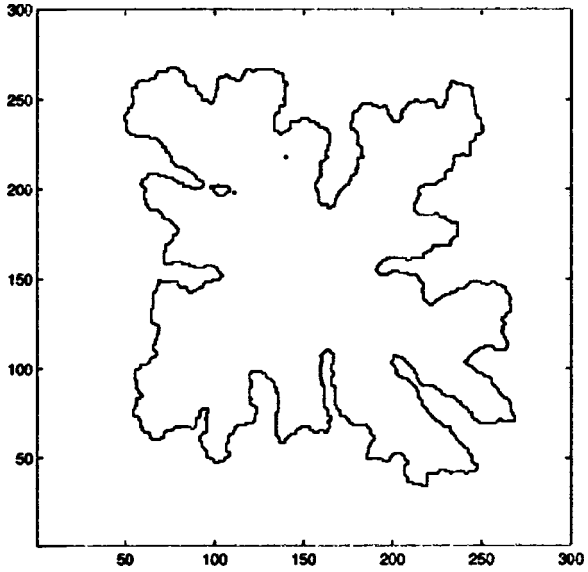

FIG. 5. Growth with $D/F=10^5$ and $\epsilon=2.5$.

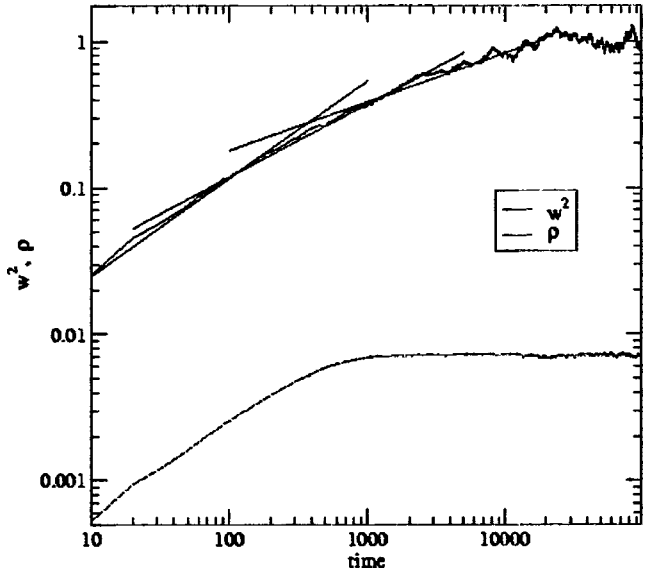

FIG. 6. Thermal roughening of a pair of steps, average over 20 simulations. Lower curve (dotted) is the average adatom density ρ. For early times, while the steps are moving, and ρ is changing, the scaling is $w^2 \propto t^{2/3}$, kinetic roughening. Later there is thermal roughening with $w^2 \propto t^{1/2}$ (evaporation-condensation kinetics) crossing over to terrace-diffusion kinetics, $w^2 \propto t^{1/3}$. The straight lines, from left to right, have slopes 2/3, 1/2, and 1/3.

In these cases $w^2 \propto t^{1/2}, t^{1/3}$, respectively. We show, in Fig. 6, $w^2(t)$ for a pair of steps one atomic layer high which cross a 100×100 terrace. We see indications of both of the expected behaviors at late times. The early time behavior is *kinetic* roughening,[21] $w^2 \propto t^{2/3}$. This is because we started with no adatoms, and, initially, the steps were retreating.

A method similar to ours is in Ref. 4. This work is in one dimension and neglects noise. A development of this approach is Ref. 5. In this work the surface is divided into two regions. Islands and terraces are treated as continuua, but a transition region is added near island edges where KMC is run. Again, the treatment is in one dimension, and we can only speculate about its performance in the cases we have treated. For the case of a complicated shape such as Fig. 4 the generalization of Ref. 5 would be considerably slowed down because the entire interior of the cluster would be treated by KMC. Further, our boundary condition, Eq. (2), takes into account repeated attachment and detachment, whereas Ref. 5 follows these processes in detail, which potentially slows its performance.

The QCMC technique should be most useful in situations where there is a large separation of time scales between the diffusion of the adatoms and fluctuations of island boundaries. Another example for which it might be used are in studies of nucleation of large islands near equilibrium on surfaces,[22] or in heteroepitaxy.

We acknowledge useful conversations with B. Orr, R. Caflisch, and J. Evans. P.S. is supported in part by NSF Grant No. DMS 0207402. P.S. and L.M.S. are supported in part by NSF Grant No. DMS 0244419. G.R. acknowledges travel grants from the Michigan Center for Theoretical Physics.

[1] J.Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic, Boston, 1993).
[2] M.F. Gyure *et al.*, Phys. Rev. E **58**, R6927 (1998).
[3] S. Chen *et al.*, J. Comput. Phys. **167**, 475 (2001).
[4] T.P. Schulze and W. E, J. Cryst. Growth **222**, 414 (2001).
[5] T.P. Schulze *et al.*, J. Comp. Physiol. **189**, 197 (2003).
[6] W.W. Mullins and R.F. Sekerka, J. Appl. Phys. **34**, 323 (1963).
[7] G.S. Bales and A. Zangwill, Phys. Rev. B **41**, 5500 (1990).
[8] T.A. Witten and L.M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[9] R.Q. Hwang *et al.*, Phys. Rev. Lett. **67**, 3279 (1991).
[10] F. Tsui *et al.*, Phys. Rev. Lett. **76**, 3164 (1996).
[11] L. Niemeyer *et al.*, Phys. Rev. Lett. **52**, 1033 (1984).
[12] E. Somfai *et al.*, Phys. Rev. Lett. **83**, 5523 (1999).
[13] C. Ratsch *et al.*, Phys. Rev. B **65**, 195403 (2002).
[14] J.S. Langer, Rev. Mod. Phys. **52**, 1 (1980).
[15] M.E.J. Newman and G.T. Barkema, *Monte Carlo Methods in Statistical Physics* (Oxford University Press, Oxford, 1999).
[16] C.H. Lam *et al.*, Phys. Rev. Lett. **89**, 216102 (2002).
[17] C. Rottman and M. Wortis, Phys. Rev. B **24**, 6274 (1981).
[18] A. Barabasi and H.E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, UK, 1995).
[19] H.C. Jeong and E.D. Williams, Surf. Sci. Rep. **34**, 175 (1999).
[20] S.V. Khare and T.L. Einstein, Phys. Rev. B **57**, 4782 (1998).
[21] M. Kardar *et al.*, Phys. Rev. Lett. **56**, 889 (1986).
[22] W. Theis and R.M. Tromp, Phys. Rev. Lett. **76**, 2770 (1996).