Devil's staircase in kinetically limited growth

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(Received 6 May 2002; published 14 October 2002)

The devil's staircase is a term used to describe surface or an equilibrium phase diagram in which various ordered facets or phases are infinitely closely packed as a function of some model parameter. A classic example is a one-dimensional Ising model [P. Bak and R. Bruinsma, Phys. Rev. Lett. **49**, 249 (1982)] wherein long-range and short-range forces compete, and the periodicity of the gaps between minority species covers all rational values. In many physical cases, crystal growth proceeds by adding surface layers that have the lowest energy, but are then frozen in place. The emerging layered structure is not the thermodynamic ground state, but is uniquely defined by the growth kinetics. It is shown that for such a system, the grown structure tends to the equilibrium ground state via a devil's staircase traversing an infinity of intermediate phases. It would be extremely difficult to deduce the simple growth law based on measurement made on such a grown structure.

DOI: 10.1103/PhysRevE.66.041605 PACS number(s): 68.55.−a, 75.10.Hk, 81.30.−t

The original devil's staircase is a footpath between Kingshouse to Kinlochleven in Scotland, so called because of the huge number of discrete steps between Glencoe and the ridge. In technical usage, the term has been used to describe situations in which the number of discrete steps within a finite range becomes formally infinite. Examples include *inter alia* the formation of facets of a crystal [2,3], antiferroelectric, smectic and lyotropic liquid crystals [4,5,3], magnetic structure in cerium monopnictides [6] and granular media [7]. Usually the staircase emerges from the interplay between long-range repulsive (antiferromagnetic) and short-range attractive (ferromagnetic) forces, with transitions between stable phases appearing as the relative strengths of the interactions are altered. The precise form of the interactions is not crucial [8].

The drive toward nanofabrication has led to a tremendous interest in growing multilayer structures. In typical methods such as molecular beam epitaxy or chemical vapor deposition, careful control of the composition of the deposited material is required to create complex artificial structures. Without such careful control nonperiodic structures tend to form. By contrast, some structures of technological interest such as quantum dots may self-assemble, and understanding the local equilibria that govern growth is crucial. In this article layer-by-layer surface growth for a simple model is shown to yield a devil's staircase structure. This suggests that for a wide class of systems the expected structure grown at zero temperature is aperiodic, and might easily be misinterpreted as disordered. This apparent disorder is not real, but arises from the locally stable structure being dependent on the thickness of the film, and there being an infinite number of locally stable structures.

Specifically, the Hamiltonian for our model is equivalent to that considered by Bak and Bruinsma [1,9],

$$H = A\sum_i \sigma_i + \sum_{ij} r_{ij}^{-\nu}\sigma_i\sigma_j . \qquad (1)$$

This model describes a situation in which each layer can be of one of the two types $\sigma_i = \pm 1$. The first term gives $\sigma_i = -1$ a lower formation energy than $\sigma_i = +1$, while the second term gives a long-ranged repulsion between like layers.

Previous work has concentrated on the devil's staircase as an equilibrium phenomenon, and searched for the thermodynamic ground state. Here, by contrast, the dynamics of growth are considered, spins being added to the system so as to minimize the energy, but then being fixed forever as further layers grow.

Many physical systems can be mapped onto this Hamiltonian: a simple example is a line of charges in an external field. The same Hamiltonian describes a situation where the σ_i represent the separations between layers rather than the layers themselves. Now the first term indicates that it costs

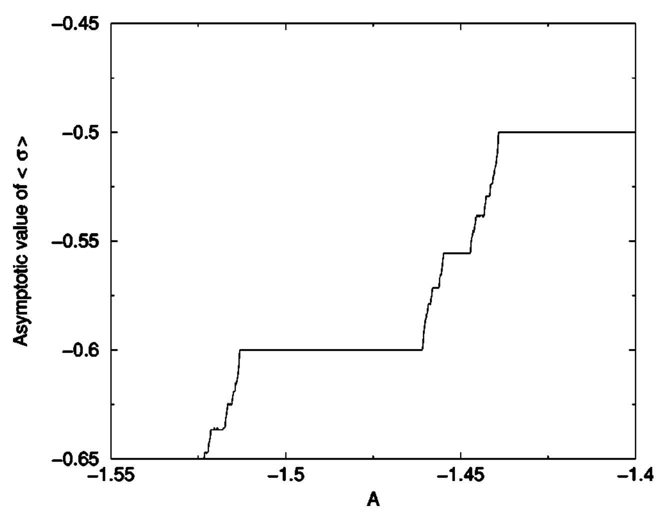

FIG. 1. Self-similar devil's staircase of phases reached asymptotically in growth with $\nu = 2$. Plotted are the value of A and the mean values of σ evaluated over the final 2520 layers of a 300 000 layer sample. 2520 $(=2\times3\times2\times5\times7\times2\times3)$ is chosen because it is commensurate with all periodicities from one to ten layers, and with 12,14,15,18,20,21, etc). For these cases the plotted value of $\langle\sigma\rangle$ is exact, for others it may be $\pm 0.04\%$.

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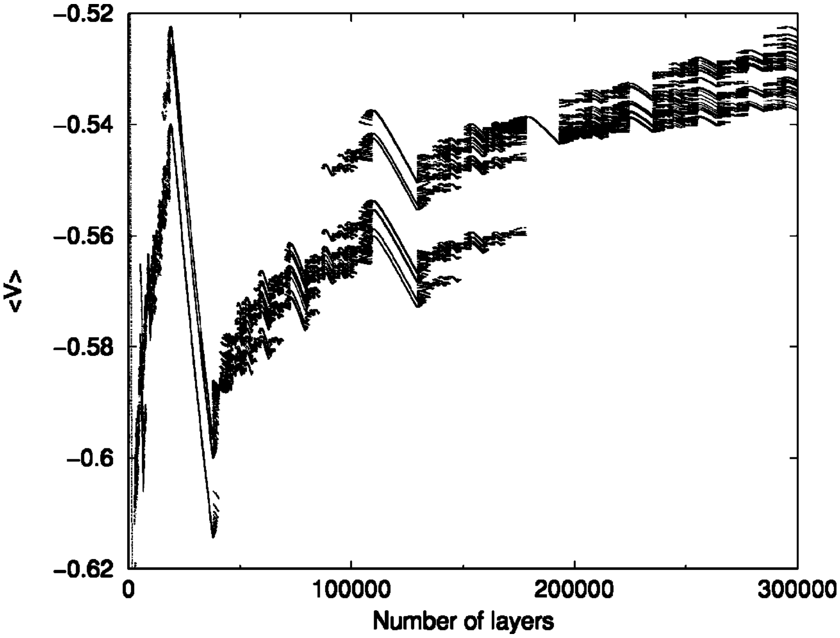

FIG. 2. Mean surface potential averaged over the preceding 72 layers before growing the ith $\sigma=+1$ layer. Highly ordered regions correspond to short-period phases which are stable over a significant range of thickness. The slope of the graph shows that even within these regions, equilibrium has not been reached and ultimately the order breaks down as a new phase is stabilized. A long-range trend towards an asymptotic value of $\langle V\rangle_{72}$ is observed. This figure generated for $\nu=1,\ A=1,\ V(0)=0$.

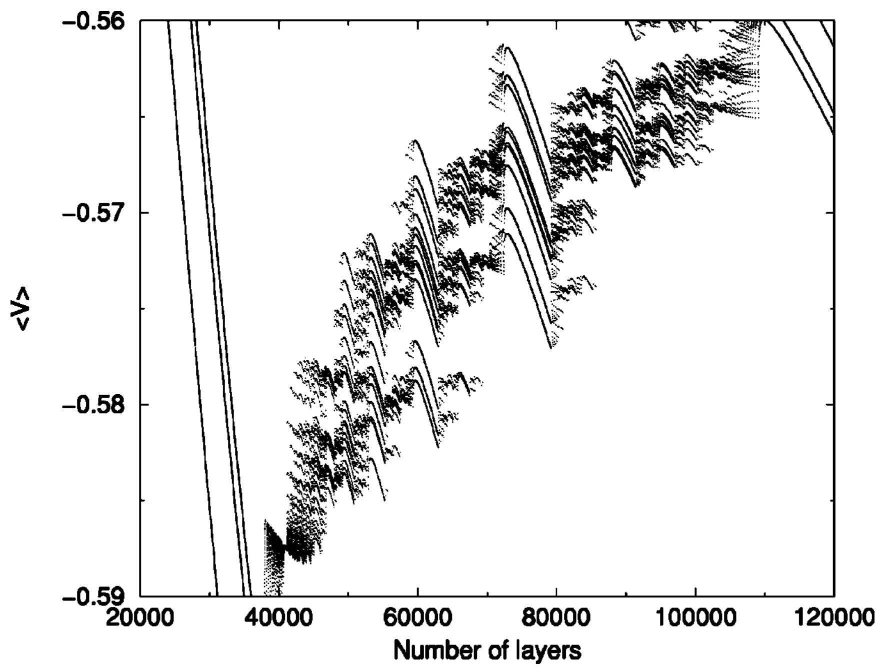

FIG. 3. Detail from Fig. 2, illustrating the ordered nature of the potential variation for a region where long-period phases are stable. The long-period repeats give rise to multiple values of $\langle V\rangle_{72}$ within the same phase, hence the multiple branches. This multiplicity can be reduced or eliminated by considering $\langle V\rangle_{2520}$ at the expense of smearing out details. In this respect the figure is not self-similar. The (arbitrarily chosen) 72-layer averaging is significant on the scale of this figure, manifesting itself for the phases that are stable over more than 72 layers as an initial increase and subsequent curvature in $\langle V\rangle_{72}$. The pure phase behavior is typically a linear decrease of $\langle V\rangle_{72}$ with N, as seen after 72 layers for those phases which are stable over a sufficiently long period.

less energy to grow either type on a similar layer, while the second term again indicates long-range repulsion (attraction) between like (unlike) layers. This might describe a system where epitaxial growth was favored, but generates a long-range strain field that needs to be periodically relieved.

Alternately, it may describe a situation such as silicon carbide growth [10,11] or stacking of close-packed planes, where each layer is locally either *ABA* or *ABC* stacked depending on its neighbors. Now σ represents the relative orientation of adjacent layers. In close-packed layer (*AB*) and interlayer (σ) notation, equivalent stacking sequences for fcc containing a growth fault are

$$\ldots A\ B\ C\ A\ B\ C\ A\ C\ B\ A\ C\ B\ A\ \ldots, \tag{2}$$

$$\cdots + + + + + + + - + + + + + + + \cdots. \tag{3}$$

Notice that a single fault of this type cannot be accommodated within periodic boundary conditions. This led Bak and Bruinsma to postulate that the actual defects in the devil's staircase are fractional, since more than one must be created together. In the growth case there is no such constraint: this is equivalent to the difference between intrinsic and extrinsic stacking faults in close-packed materials (which can arise from removal or insertion of a plane) and growth defects (basal plane twins) which reverse the sense of stacking and can be generated only by finite shear of the entire sample or during growth.

Finally, the model can describe a simple history-dependent system, where the state of the system depends on a sum over its historical values. In this case the "layer number" should be interpreted as a time rather than space dimension.

For the growth dynamics, one simply considers adding the $(n+1)$th layer to the preexisting *n* layers with whichever spin reduces the energy. This can be determined entirely by the sign of the local potential at the position of the next layer V_{n+1}:

$$\Delta E_{n+1} = V_{n+1}\sigma_{n+1} = \left(A + \sum_{j=1}^{N} r_{ij}^{-\nu}\sigma_j \right)\sigma_i . \tag{4}$$

In zero-temperature case considered here, if V_{n+1} is positive, the next added layer $\sigma_{n+1} = -1$, otherwise $\sigma_{n+1} = +1$. Furthermore, the final structure is uniquely defined and while it may appear random, it has zero entropy.

At thermodynamic equilibrium, or asymptotically for the growth dynamics, this model [Eq. (1)] has two simple limiting cases. For weak long-range interactions defined by

$$A > \left[\sum_{n=1}^{\infty} n^{-\nu} \right] = \zeta(\nu), \tag{5}$$

$\sigma_n = -1$ for all *n*, meanwhile for small *A* alternating behavior $\sigma_n = (-1)^n$ is observed. For intermediate values of *A*, the devil's staircase of phases is recovered in the asymptotic limit (Fig. 1) [1].

In the case of growth, we find that a convenient parameter to monitor is $\langle V \rangle_m$, the rolling mean value of the potential between V_{n-m} and V_n wherever a layer type $\sigma_n = +1$ is grown. For the case of $\nu = 2$ the asymptotic value of $\langle V \rangle_{2520}$ plotted against *A* picks out the conventional devil's staircase behavior (Fig. 1).

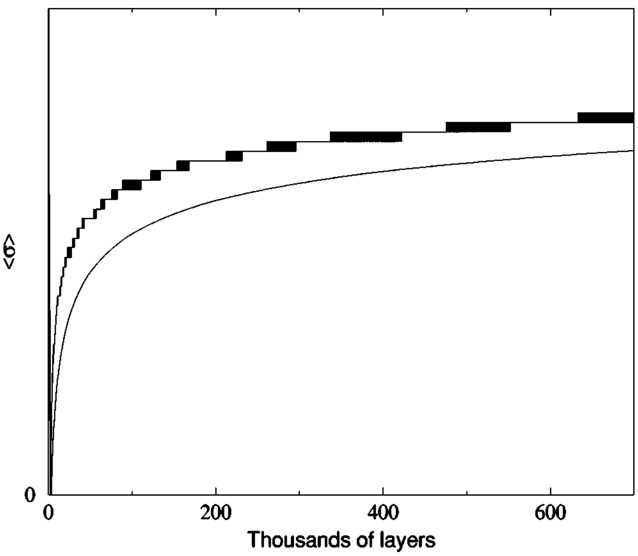

FIG. 4. Mean value of σ for $\nu = 1$, $A = 1$. The upper line is averaged over the preceding 2520 layers, picking out as straight lines phases of repeat period as in Fig. 1. Transitions between these short-period phases are characterized by longer-period phases, which are shown by thick black lines (actually representing a rapid fluctuation between $K/2520$ and $(K+1)/2520$ for integer K). The lower line is averaged over the whole layer, and shows the very slow monotonic growth of $\langle \sigma \rangle$ towards the asymptotic value of $\langle \sigma \rangle = 0$). The increase in the mean value of $1/\langle \sigma \rangle$ is logarithmic, a reasonable fit to the graph being $\langle \sigma \rangle = [7 - 2.9 \ln N]^{-1}$. For higher values of *A* the convergence of $\langle \sigma \rangle \rightarrow 0$ is even slower. For $\nu > 1$ the asymptotic value of $\langle \sigma \rangle$ is nonzero: it is a phase from the devil's staircase dependent upon *A*.

Our interest lies in the convergence of the structure with layer number—physically how thick a film must grow to recover bulk behavior. Again this can be monitored using $\langle V \rangle_m$, now plotted against the layer number. For $\nu = 2$ the growth converges fairly rapidly to the equilibrium value, the effective screening of the surface is fast compared with the integer layer spacing. For smaller ν convergence is slow: Figures 2–4 show the case of $\nu = 1$, $A = 1$, now the screening is sufficiently slow that a wide range of different phases from the "devil's staircase" are actually observed over a number of layers.

The actual phases and "screening" effect are illustrated by the running average of the ratio of $\sigma = +1$ to $\sigma = -1$ over the previous 72 layers (72 is chosen such that phases with periods 2,3,4,6,8,9, etc., will give a constant value). To further reduce the oscillation, the ratio is printed out only at layers with $\sigma = +1$. Substantial single phase regions can be seen, together with shorter transitional regions. The overall trend towards a limiting value can be seen.

Each phase is stable only over a finite number of layers. Since the range of stability is inversely proportional to the period of the structure [1], the thickness over which some long-period structures are stable will be shorter than the periodic repeat distance of these structures. Consequently, they cannot be identified unambiguously.

The long-term trend of Fig. 2 is toward $\langle V\rangle_m = -0.5$. This corresponds to equal numbers of $\sigma = \pm 1$ which give a mean field value of $V=0$ averaged over all layers, and $\langle V\rangle_m = -A/2 = -0.5$ averaged over the $\sigma = +1$ layers only. A very curious phenomenon observed in Fig. 2 is that the ordered phases show *antiscreening* behavior: the mean value of $\langle V\rangle_m$ moves away from the asymptotic value for most of the range of the ordered phase. Thus while the overall trend is an asymptotic increase of $\langle V\rangle_m$, within any given phase $d\langle V\rangle_m/dN$ is negative [12]. Evolution towards the asymptote is achieved via the boundaries between the phases, rather than the screening by the phases themselves.

In mapping onto a real growth process, the value of A is determined by the material being deposited; however, it may be possible by choice of substrate or external applied field to control the initial value of the potential. By doing so, the density profile of $\sigma = +1$ may be varied. This is not straightforward however: if the initial condition is compatible with the equilibrium structure, a perfect multilayer can be grown; if not, the concentration will traverse all possible phases with $\sigma = +1$ density intermediate between the starting and equilibrium ones. There are an infinity of these phases, but their thickness must take an integer value, thus not all phases can actually be observed. If the interlayer spacing is taken to be of atomic dimension, a perfectly grown (i.e., zero T, zero entropy) film of even a millimeter thickness may not reach equilibrium and will appear disordered to any experimental probe. Of course, in a real system thermal effects and imperfections in growth will cause additional disorder—the central result of the present work is to show that even when all experimental imperfections are removed, growth kinetics *still* results in a structure that will appear disordered.

By interpreting the layer number N as a time rather than a thickness, this type of growth-kinetic model also provides a simple model of history dependence. In many social phenomena, decisions are made for one of two courses of action based on the evidence of the past behavior with more recent evidence having a stronger weight [13]. Here the model already contains enough complexity to behave counterintuitively: the long-term trend of increasing $\langle V\rangle_m$ is opposite in sign to the $d\langle V\rangle_m/dN$ measured over the stable phases, despite the fact that formally the devil's staircase provides a stable phase at all N, and by implication $d\langle V\rangle_m/dN$ is negative everywhere. Of course, the spin-Ising model is a gross oversimplification of any real decision making process: this only serves to emphasize the nontrivial relation between the model and its behavior, and the difficulty for measurement when $d\langle V\rangle_m/dN$ is negative everywhere while $\Delta V/\Delta N$ is positive.

In sum, the growth kinetics of a simple model exhibiting long-range antiferromagnetic and short-range ferromagnetic ordering have been studied. This has been shown to exhibit logarithmically slow equilibration to the equilibrium structure, passing through a formally infinite number of intermediate phases that form a devil's staircase.

The author would like to thank D. Srolovitz and J. Rickman for helpful discussions and hospitality at Princeton University, and the Fulbright Foundation for support.

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[12] The continuous limiting case $\langle V\rangle_1$ is a function whose derivative is negative everywhere, yet which increases to an asymptote by virtue of discontinuities at the (infinity of) phase boundaries.
[13] Imagine the dilemma of a voter in a country with only two political parties. The voter's personal preference (measured by A) is tempered by a belief that any party too long in government becomes corrupt (measured by ν). A study of the voting pattern is unlikely to discern this determination decision-making process, concluding instead that the pattern is random.