

## A Model of Quasicrystal Growth

Dieter Joseph and Veit Elser

*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501*

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Entropically stabilized quasicrystals are usually modeled as equilibrium ensembles of random tilings. In several models, such as the two-dimensional square-triangle tiling studied here, the corresponding kinetics may be very slow because a large number of tiles must be rearranged at each step through the ensemble. Here we consider a simple growth model that generates a single element of the square-triangle tiling ensemble. Even though tile rearrangements occur only at the growth surface, in the limit of slow growth one obtains a structure that is representative of the equilibrium ensemble. [S0031-9007(97)03773-3]

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The debate concerning the stability of quasicrystals continues to revolve about the relative roles of energy and entropy [1–3]. This debate applies to a description of structure based on tiles representing the short range structure in the material. The energetic mechanism postulates that the interactions among the tiles are such as to favor a unique quasiperiodic ground state. The entropic mechanism, on the other hand, neglects energy differences among tile arrangements; there is no unique quasiperiodic state but quasiperiodicity in the long range order is a property of typical elements of the ensemble of “random tilings.” The two viewpoints also differ markedly on the issue of growth. For an energetically stabilized quasicrystal, growth gets in the way of perfection and is held accountable for the phason-disorder observed in even the highest quality quasicrystals. Taking the entropic viewpoint, we argue in this Letter the opposite: that, in fact, growth may be fundamental in providing a pathway to the entropically stabilized state.

To test our ideas we have focussed on the ensemble of two-dimensional square-triangle tilings [4]. Two tiles, a square and an equilateral triangle with common edge length  $a$ , are joined edge to edge so as to tile regions of the plane. Seen as a collection of vertices joined by edges all having the same length and only six possible orientations, any element of the ensemble corresponds to the projection of a corresponding set of vertices from a four-dimensional lattice. A tiling thus corresponds to a particular embedding of a surface in this space. More is known about this ensemble of surfaces than any other random-tiling system and explains our choice of model. In particular, exact values of the entropy per vertex  $s_0$  and the phason stiffness  $\kappa$  were found by Widom [5] and Kalugin [6] using Bethe Ansatz methods. Both quantities apply to the thermodynamic limit of the equilibrium ensemble where each tiling contributes with the same weight.

Another reason for choosing the square-triangle tiling is the difficulty of moving through the ensemble. A typical move consists of a zipperlike operation performed on a closed loop of tiles [4]. Since the loops can be quite long

and the tile vertices usually represent entire clusters of atoms, such rearrangements (unless mediated by defects) can be ruled out in a real quasicrystal. Our study of a growth model was motivated by the idea that a sufficiently random growth process might be able to generate a single element of the equilibrium ensemble while avoiding the slow kinetics of zippers.

The energetics of our model only distinguishes between interior and boundary vertices of the tiling. Thus at each vertex we introduce a variable  $\theta_i$  which measures the total angle subtended by complete tiles (squares and triangles). Since these angles are always some integer multiple of  $2\pi/12$ , we rescale  $\theta_i$  to be an integer in the set  $0, \dots, 12$ . The energy of a tiling is then given by the Hamiltonian

$$H = \sum_i \mu - \theta_i. \quad (1)$$

The sum extends over all vertices of the tiling and  $\mu$  represents the chemical potential of the atoms forming a cluster (at some vertex) relative to the chemical potential of the same atoms in the liquid phase. We note that all interior vertices, regardless of the tile arrangement, have the same energy:  $\mu - 12$ . The bulk free energy is minimized when the tile arrangements have the maximum entropy. Since this is known from the equilibrium ensemble, the minimum bulk free energy per vertex in our model is given by

$$f_{\min} = \mu - 12 - Ts_0, \quad (2)$$

where  $T$  is the temperature. This shows that a tiling could grow provided the parameters  $\mu$  and  $T$  are chosen so that  $f_{\min} < 0$ . Moreover, we note that growth near the boundary of this region in parameter space is only possible if the tiling takes advantage of the entropy maximizing statistical properties of the equilibrium ensemble. This approach is significantly different from other growth models like in [7] because it fully respects detailed balance and enables real thermodynamics.

To complete the description of our model we need to define our ensemble and the kinetics within that ensemble. The most primitive definition that suits our purposes

is to consider all finite graphs with the properties that (i) all edges have length  $a$  and relative angles a multiple of  $2\pi/12$  and (ii) the minimum distance between any two vertices is  $a$ . The union of a graph and the interiors of all squares and triangles (of side  $a$ ) it may contain will be called a “tile cluster.” For technical reasons we restrict our ensemble to include only tile clusters having a connected boundary (topological disks). Had we insisted on only connectedness of the cluster and allowed interior holes, for example, then moves that change the number of boundary curves would have to inspect the tiling globally to check that it was not getting disconnected. In the regime of slow growth at low or medium temperatures considered below, this restriction has a negligible effect on the kinetics.

The moves within the ensemble involve either deleting a boundary vertex or adding a vertex in the cluster exterior. Lists of the removable and potentially new vertices are tabulated and we imagine each being subject to having its status changed within a time interval  $\tau_c$ . Physically,  $\tau_c$  corresponds to the time needed for an atomic cluster to melt or crystallize from the melt [8]. The probability of changing the status of a vertex is determined by the Metropolis rule applied to the Hamiltonian (1). Our simulations considered two topologies of the ambient space: plane and cylinder. For growth in the plane the initial seed cluster was a circular patch taken from a quasiperiodic square-triangle tiling; later, circular patches were excised from clusters grown with the appropriate parameters and used as seeds. For growth on the cylinder, a quasiperiodic boundary curve that spanned the circumference was used as a seed. Inevitably, simulations on the cylinder introduce a small average phason strain due to the periodic boundary conditions.

Simulations in the plane confirmed our basic expectations. At sufficiently low temperatures ( $T \lesssim 4$ ) the surface tension is positive and the clusters have a compact shape at early times. Aside from a small correction, scaling as the mean curvature of the cluster surface, we find that the boundary of the region in parameter space where growth occurs coincides with the condition  $f_{\min} = 0$ . Simulations on the cylinder, where surface curvature is absent, are consistent with the exact value  $s_0 = \ln(2^2 3^3) - 2\sqrt{3} \ln(2 + \sqrt{3}) \simeq 0.12006$  [5,6]. Extrapolating to zero growth velocity we find  $s_0 = 0.1200(5)$ . In the limit of very slow growth the fluctuations of the surface are just as important as its average drift and the tiling is continuously being disassembled and reassembled in different random ways. Since the maximum entropy state appears to be accessible without the need for complicated “zipper” moves, our method should prove useful in determining  $s_0$  in models where the analogs of zippers are poorly understood.

After a sufficiently long time the growth morphology appears dendritic due to the formation of “tears” (Fig. 1) [8]. Tears represent discontinuities in the corresponding

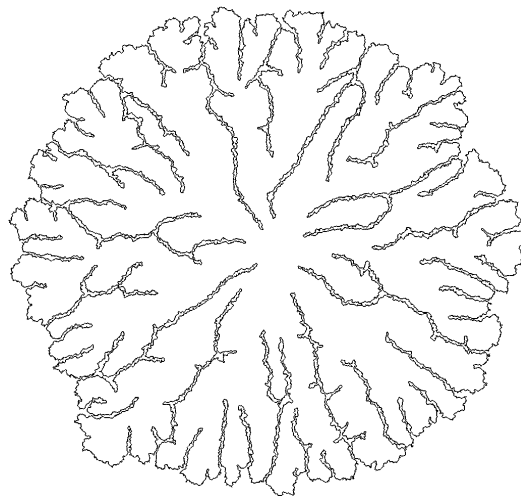


FIG. 1. Surface of a tile cluster containing  $1.8 \times 10^5$  vertices. The relatively high growth velocity in this simulation ( $T = 3$ ,  $\mu = 11.50$ ) leads to a high density of tears.

embedded surface, i.e., a jump in the  $\mathbf{x}_\perp$  coordinates that are orthogonal to the tiling plane into which the surface is normally projected. In physical terms, the two sides of the tear cannot be sewn together because a new vertex placed in the gap would be too close to an already existing vertex. On the other hand, as the discontinuity in  $\mathbf{x}_\perp$  increases, an ever smaller relative displacement of the two sides of the tear is needed to allow closure. In real quasicrystals tears would thus mend, forming dislocations. Whether mended or not, tears limit the long range order in the quasicrystal and must be eliminated if our model is to apply to the highest quality quasicrystals.

The mean separation of tears along the surface of the growing cluster can be estimated by measuring the fraction of surface vertices,  $f_{\text{surf}}$ . In the asymptotic regime when the cluster is fragmented into many fingers of width  $\lambda_{\text{tear}}$ ,  $f_{\text{surf}} \propto \lambda_{\text{tear}}^{-1}$ . Our simulations at fixed  $T$  and  $\mu$  near  $\mu_{\max} = 12 + Ts_0$  find (Fig. 2)

$$\lambda_{\text{tear}} \sim (\mu_{\max} - \mu)^{-1}. \quad (3)$$

This behavior can be understood in terms of a coupling between the local growth velocity and the  $\mathbf{x}_\perp$  degrees of freedom, or phasons, of the corresponding embedded surface. Suppose a piece of the boundary of the embedded surface is dominated by one phason mode of large amplitude and wavelength  $\lambda$  along the boundary (Fig. 3). The entropically generated phason stiffness will relax this mode by diffusion of tiles along the surface with a relaxation time  $\tau_\lambda \sim \lambda^2/D$  in the limit of large  $\lambda$ . The “surface phason” diffusion constant  $D$  has a nonsingular behavior for  $\mu$  near  $\mu_{\max}$ . The growth velocity will vary along the boundary, being smallest where the phason gradient is largest. This again is an entropic effect: A finite phason gradient lowers the entropy thereby increasing the local free energy density and decreasing the local growth velocity. If  $v$  is the average (positive)

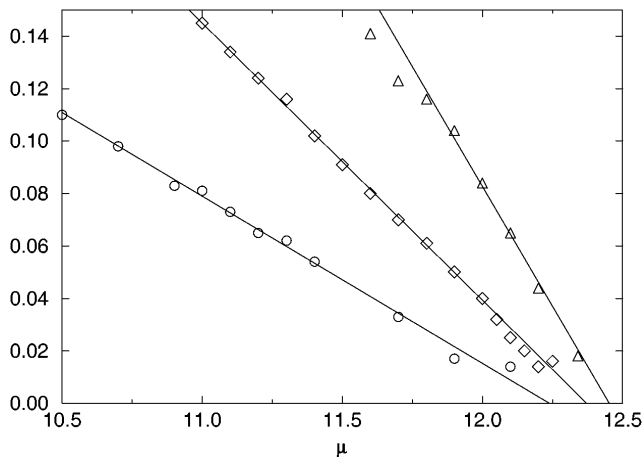


FIG. 2. Fraction of surface vertices as a function of chemical potential  $\mu$  for three temperatures: ( $\circ$ )  $T = 2$ , ( $\diamond$ )  $T = 3$ , and ( $\triangle$ )  $T = 3.5$ . From the proportionality  $f_{\text{surf}} \propto \lambda_{\text{tear}}^{-1}$ , one infers that the mean separation of tears diverges as  $\mu \rightarrow \mu_{\text{max}}$ .

growth velocity, the variation in the local growth velocity can be of order  $v$  if the phason amplitude is sufficiently great. Thus the point of maximum phason gradient will form the nucleus of a tear unless  $v\tau_\lambda \ll \lambda$ . Conversely, one expects tears to nucleate on a length scale  $\lambda$  when  $v \sim \lambda/\tau_\lambda \sim D/\lambda$ . Combining this with the proportionality between  $\mu_{\text{max}} - \mu$  and the average growth velocity one obtains Eq. (3). The  $\mu_{\text{max}}$  determined by this kind of measurement yields the estimate  $s_0 = 0.120(3)$ .

By choosing  $\mu$  very close to  $\mu_{\text{max}}$  we have been able to grow tile clusters of over  $10^5$  vertices that were completely free of tears. Assuming that the same disordering mechanism and scaling law (3) applies in three dimensions, one can ask how slowly a quasicrystal should be grown so that no tears (dislocations) are present in the entire sample. Figure 4 shows part of a cluster grown in the cylindrical topology. The strip has width

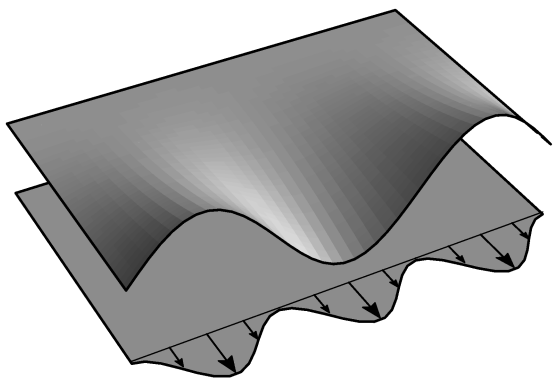


FIG. 3. Relationship between phason gradients near the surface of a growing tile cluster and variations in the local growth velocity (arrows in the lower part). Only one component of the phason coordinate (upper part) can be represented in this three-dimensional sketch.

107a and for the parameters chosen there was typically just one tear. In terms of our microscopic time scale the growth velocity was measured to be  $0.003(a/\tau_c)$ . Using the rough estimate  $\tau_c \approx 10^{-9}$  sec [8] and a cluster-cluster separation of  $a = 5 \text{ \AA}$ , the velocity required to achieve  $\lambda_{\text{tear}} \approx 1 \text{ mm}$  extrapolates to 0.3 mm/h.

The power spectrum of phason fluctuations provides a more critical comparison with the equilibrium ensemble. Denoting the Fourier amplitude at wave vector  $\mathbf{q}$  of the phason coordinates by  $\mathbf{x}_\perp(\mathbf{q})$ , the hydrodynamical theory of the equilibrium ensemble predicts that the two components of  $\mathbf{x}_\perp(\mathbf{q})$  are independent, Gaussian-distributed random variables with variance [3]

$$\langle |\mathbf{x}_\perp(\mathbf{q})|^2 \rangle = (\kappa_\mu |\mathbf{q}|^2)^{-1} (|\mathbf{q}| \rightarrow 0). \quad (4)$$

Following the conventions of Ref. [4], the phason stiffness constant (determined by Bethe Ansatz [5,6]) has the value  $\kappa_\mu = 2\sqrt{3} - 3 \approx 0.464$ . To check whether the phason fluctuations in the grown tilings approach the equilibrium spectrum in the limit of slow growth, we fixed the temperature  $T = 3$  and grew a sequence of samples in the cylindrical topology at values of  $\mu$  that approached  $\mu_{\text{max}} = 12.360$ . The periodic dimension of the tilings was chosen small enough,  $L = 107a$ , so that no tears were formed at even the lowest values of  $\mu$ . Each sample was grown to a length of about  $4L$ , thereby minimizing the influence of the seed. Phason amplitudes  $\mathbf{x}_\perp(\mathbf{q})$  were measured for all  $|\mathbf{q}|$  between upper and lower momentum cutoffs,  $q_{\text{max}} = 25(2\pi/L)$  and  $q_{\text{min}} = 2\pi/L$ . Although there are longer wavelength modes along the growth direction, these reflect the statistics of a one-dimensional random walk and therefore provide no useful information. In analyzing our data, we noted that in the equilibrium

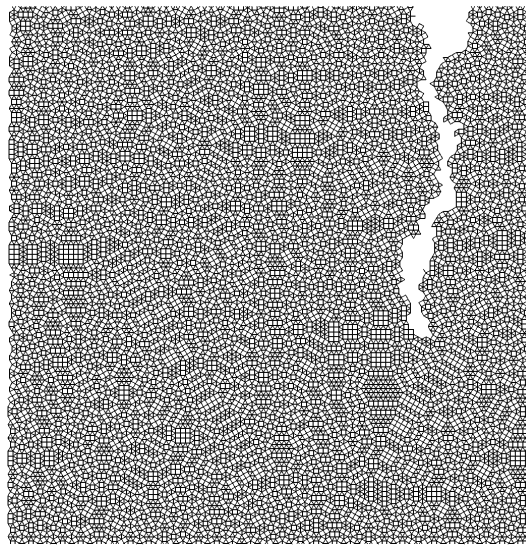


FIG. 4. Detail of a tiling grown on the cylinder in the regime of moderate growth velocities ( $T = 3$ ,  $\mu = 12.225$ ,  $L = 107a$ ) with one tear. The growth direction is vertical. The nucleation of the tear in a region of high phason strain can clearly be seen.

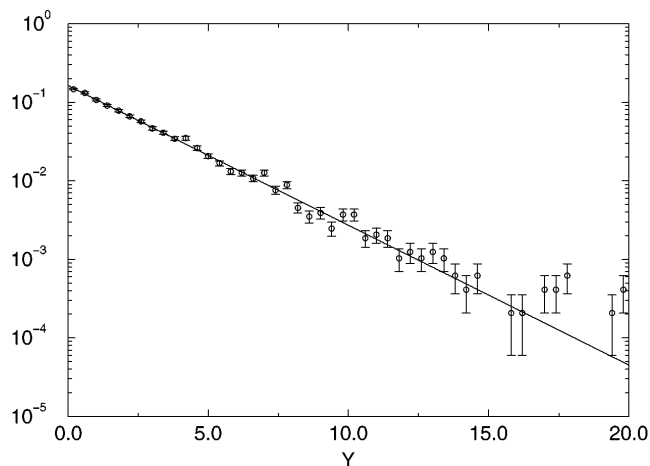


FIG. 5. Probability distribution of  $Y = |\mathbf{q}|^2 |\mathbf{x}_\perp(\mathbf{q})|^2$  and a least squares fit to determine  $\kappa_\mu$  at  $T = 3$ ,  $\mu = 12.345$ . The results are summarized in Table I.

ensemble the random variable  $|\mathbf{q}|^2 |\mathbf{x}_\perp(\mathbf{q})|^2$  has an exponential distribution with decay constant given by  $\kappa_\mu$ . A typical distribution of the same random variable obtained from one of our grown samples is shown in Fig. 5. The slope of the data yields  $\kappa_\mu$ ; values for each of the grown samples are given in Table I. We see that the phason stiffnesses of the grown samples are always smaller but, as expected, appear to approach the equilibrium value as the growth velocity tends to zero.

In summary, our simulations support the proposition that the unique, maximum entropy state of a random tiling quasicrystal is accessible through growth alone, without the need for complex tile-rearrangement processes in the bulk. The slow kinetics of bulk rearrangements is, in fact, a blessing, since otherwise the entropically stabilized quasicrystal would transform to a crystal at low temperature.

TABLE I. Phason stiffness constant  $\kappa_\mu$  as a function of the chemical potential  $\mu$  of samples grown on the cylinder at  $T = 3$ . The errors given represent fitting errors.

$\mu$	$\kappa_\mu$	$\mu$	$\kappa_\mu$	$\mu$	$\kappa_\mu$
12.300	0.34(2)	12.330	0.37(2)	12.345	0.41(2)
12.310	0.35(2)	12.335	0.37(2)	12.350	0.44(2)
12.320	0.36(2)	12.340	0.39(2)		

Our simulations also suggest that “tearing” of the tiling’s embedded surface (and subsequent formation of dislocations) is a principal disordering mechanism.

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