Growth of Hard-Sphere Models with Two Different Sizes: Can a Quasicrystal Result?

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We define a growth model analogous to the Eden model, but with two types of atoms interacting through hard-sphere potentials. In some two-dimensional cases, these models generate structures which are neither periodic nor quasiperiodic, but have a characteristic topology that distinguishes them from glasses. This topology is analogous to that of Penrose lattices. Locally, the structure is of the Hendricks-Teller type: alternation of strips of fat and skinny Penrose rhombi.

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Quasicrystals are generally characterized by the following properties[1-3]: (i) a diffraction spectrum consisting of sharp Bragg peaks which have a symmetry forbidden in crystals—in practice, a fivefold or an icosahedral symmetry; (ii) orientational order; (iii) a topological order to be described more in detail below. Property (i) is called quasiperiodicity. Other authors[4-6] treat quasicrystals rather as glasses with a strong short-range order.

Landau theories which describe the formation of quasicrystals *at equilibrium* have been given by Bak[2] and by Mermin,[3] and Monte Carlo simulations of Widom, Strandberg, and Swendsen[7] also indicate that quasicrystals can exist at equilibrium. However, most of the quasicrystals are not stable at any temperature and form as a result of some quenching process. The motivation of the present work is to investigate whether some growth process can give rise to quasicrystals. Our growth model has some analogy with quenching because each atom becomes frozen as soon as it sticks to the growing cluster. Only the sticking process is dynamical and involves the minimization of some energy.

Our model is a two-dimensional one. We consider two types of "atoms," big and small (B and s). The distance between the centers of the atoms of a BB, Bs, or ss pair has a minimal value of d_{BB}, d_{Bs}, or d_{ss}, respectively. A pair of atoms separated by the minimal distance are called neighbors.

If the ratios

$$x=d_{ss}/d_{Bs}, \quad Y=d_{BB}/d_{Bs} \tag{1}$$

are not appropriately chosen, the growth of such a mixture gives rise to an amorphous structure,[6] or to two crystals, B and s, respectively. An appropriate choice of x and Y was obtained from a decoration of Penrose tiles [Figs. 1(a) and 1(b)] by Lançon and Billard[8]:

$$x=2\sin(\pi/10), \quad Y=2\sin(\pi/5). \tag{2}$$

We explicitly exclude the possibility for three identical atoms (B or s) to be neighbors, since the weak commensurability of $\pi/3$ with $\pi/5$ would drastically reduce the probability to form anything else than a glass, or a B crystal plus an s crystal. Thus, we require the plane to be filled by BBs and Bss triangles in which any two corners are neighbors and have the required distance. This excludes the geometry of Fig. 1(c) in the decoration of a Penrose lattice. Any Penrose lattice generated according to the rules of Fig. 4 of Ref. 1 can be decorated without the configuration shown in Fig. 1(c) occurring. The proof can be given in two steps. One first shows that a fat rhombus can only touch two other fat rhombi. Therefore, fat rhombi form either loops or stars which are isolated from one another by thin rhombi. Then one proves that any loop or star formed by fat rhombi can be decorated avoiding the configuration of Fig. 1(c), and this completes the proof.

In contrast with another decoration of Penrose tiles proposed by Elser and Henley,[9] our model defined by (2) was used by Lançon and Billard,[8] and by Widom, Strandberg, and Swendsen.[7] However, we generate the structure neither by the projection method (as in Ref. 8) nor by the Monte Carlo method (as in Ref. 7), but by a

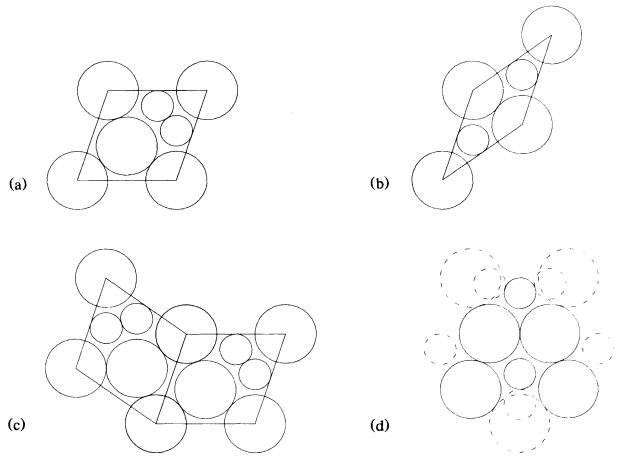

FIG. 1. (a),(b) Decoration of the two rhombi quasi unit cells of a Penrose lattice. (c) A forbidden decoration. (d) A small cluster (solid atoms) and some places (dashed atoms) where a new atom might be stuck.

growth model analogous to the Eden model.[10] We define an energy, which is the sum of pair energies W_{BB}, W_{Bs}, and W_{ss} (all assumed negative) respectively multiplied by the number of corresponding pairs of nearest neighbors. There is a growing cluster and one atom at a time is allowed to stick to the cluster, and once it has stuck it does not move any longer. The atom which sticks and the place where it sticks are chosen to minimize the energy. Figure 1(d) shows a small cluster and some possible places where an atom might stick to the cluster. If these requirements can be satisfied in more than one way, the atom to stick and its place are randomly chosen. The growth is done "layer by layer." When a layer is completed a new set of all possible sticking places is considered. When all possible sticking places of this set are filled this layer is completed. Physically, this procedure expresses the fact that the flux of particles is rather uniform and obliges the growth to be rather uniform too. Note a rather unphysical oversimplification in our model: The chemical potential of the two species is not taken into account.

The only candidates to the title of quasicrystals are the structures which completely fill the space with triangles of nearest neighbors. This is not the kind of structure *generally* obtained with our growth procedure. Generally, tears are generated. Figure 2(a) shows the result of a computer simulation for a growth layer after layer for atoms (B and s). It *displays tears* and should be regarded as an amorphous material.

However, if $W_B = W_{BB}/W_{Bs}$ and $W_s = W_{ss}/W_{Bs}$ are chosen in a certain range, defined by Eq. (3) below, the computer simulation does generate structures *without tears* [Fig. 2(b)]. These structures are not amorphous. They are not crystalline either. However, they are *locally* more anisotropic than a quasicrystal is expected to be. We suspect that the Al_6CuLi_3 quasicrystals recently obtained by Dubost *et al.*[11] might have a local anisotropy similar to our Fig. 2(b). Actually they show plane faces which would be favored by such an anisotropy. Elser[12] also observed some anisotropy (although much weaker) in his growth simulation. The appropriate conditions for W_B and W_s to generate structure without tears are

$$W_s < W_B < 1 < 2W_B - W_s. \tag{3}$$

The proof of these conditions will be published elsewhere.

It turns out that the structure of Fig. 2(b), obtained by computer simulation, can be interpreted if one excludes a small region around the center. It is appropriate to distinguish twenty sectors separated by twenty lines starting from the origin, and which will be described later. Within each sector the structure may be viewed as an alternation of strips of two crystal forms separated by parallel boundaries. One of these crystal structures is made of alternating rows of big and small atoms and can be tiled by skinny Penrose rhombi (Fig. 3) and will be called *skinny*. In the other crystal structure, big atoms form stretched hexagons, each of which contains two small atoms. This crystal lattice can be tiled by fat Penrose rhombi and will be called *fat*.

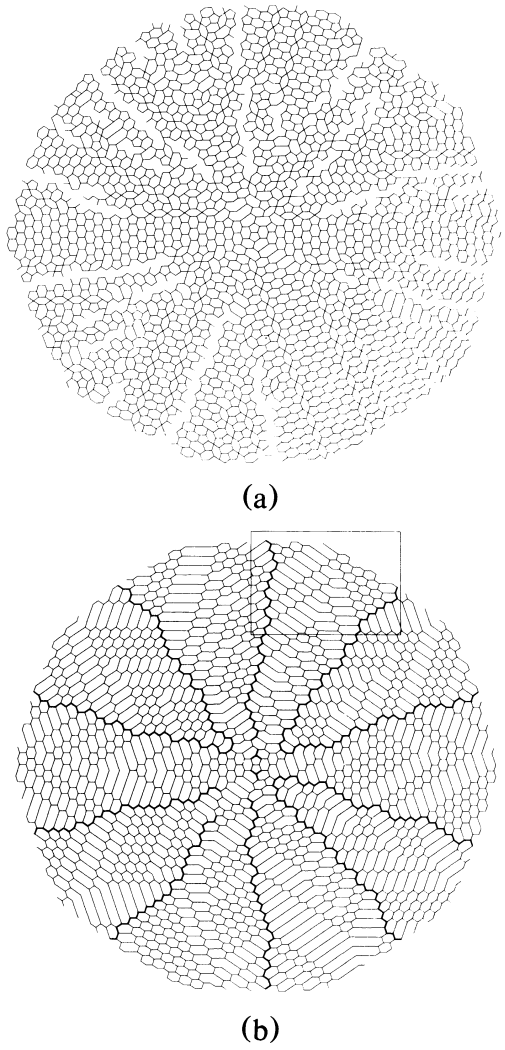

FIG. 2. Results of a computer simulation for a growth layer after layer. The lines drawn are between the centers of neighboring big atoms only ($W_s \equiv W_{ss}/W_{sB}$ and $W_B \equiv W_{BB}/W_{sB}$). (a) $W_s = 1$, $W_B = 2$; (b) $W_s = \frac{1}{7}$, $W_B = \frac{5}{7}$. The heavy lines in (b) are the freedom lines, and contain the only degrees of freedom in the growth far from the center. The boxed region in (b) is shown in Fig. 3.

Each sector is limited by two different types of frontiers on its two sides. One frontier, hereafter called a "freedom line," contains *all* degrees of freedom. With every two new layers this line (Fig. 3) can either go straight or turn. This choice corresponds to the choice between completing the environment of a big black atom seen in Fig. 3 by a big atom at the right and a small atom at the left, or vice versa. The two possibilities have

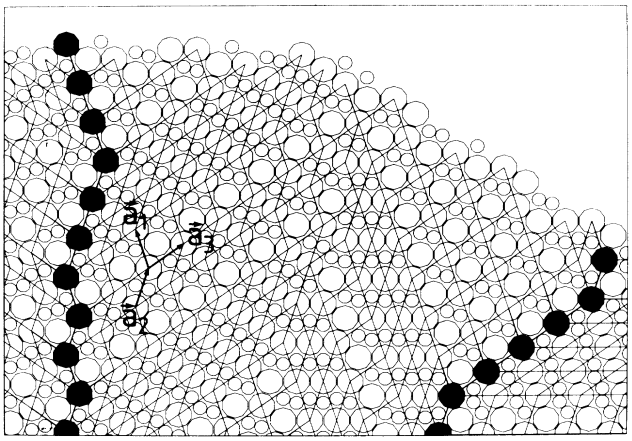

FIG. 3. An enlarged picture of the boxed region in Fig. 2(b), showing both large and small atoms. The rhombi drawn correspond to those used in Figs. 1(a) and 1(b). The second and third freedom lines in Fig. 2(b) are indicated by black atoms, which emit strips of fat or skinny rhombi. The junction line is where a strip of thin rhombi emitted from the right side of the left freedom line meets a strip of thin rhombi emitted from the left side of the right freedom line.

exactly the same energy, so that the probabilities for a freedom line to go straight or to turn are equal. A straight freedom line has skinny rhombi on one side and fat rhombi on the other side. When it turns, the respective position of both crystal forms changes. The orientation of the jth freedom line fluctuates between $\pi j/5$ and $\pi(j-1)/5$ so that it cannot meet the $(j+1)$th or the $(j-1)$th freedom line. The other frontier is a "junction line" where the strips of fat and skinny rhombi emanating from the jth and $(j+1)$th freedom line meet. The structure within each sector is a random alternation of strips of fat and skinny rhombi. This type of random structure was first considered by Hendricks and Teller.[13]

The position $\mathbf{R}$ of any big atom of Fig. 2(b) can be written as

$$\mathbf{R}=\sum_{j=1}^{4} p_j \mathbf{e}_j, \tag{4}$$

where

$$\mathbf{e}_j=[2/(a\cos\pi/5)](\cos 2\pi j/5,\ \sin 2\pi j/5).$$

Here, the p_j's are uniquely determined for any given point $\mathbf{R}$. Property (4) is also satisfied by Penrose lattices. This well-known[14,15] relation (4) implies that Fig. 2(b) is the projection of a slice of a four-dimensional lattice, because for each j $(1\le j\le 4)$ one can define a vector $\mathbf{e}_j^{\perp}$ in a plane perpendicular to the physical plane, such that the four four-dimensional vectors $(\mathbf{e}_j,\mathbf{e}_j^{\perp})$ are linearly independent.

If we focus our attention on one sector, we observe that all rhombi have two sides equal to a vector which we call $\mathbf{a}_3$ and other sides equal to two other vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ for fat and skinny rhombi, respectively (Fig. 3). Within this sector, Eq. (4) can be simplified to

$$\mathbf{R}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3 \tag{5}$$

with integers n_i uniquely determined for a given big atom. The same argument as before shows that the structure which constitutes each sector can be considered as a projection of a piece of a three-dimensional Bravais lattice with basis vectors $(\mathbf{a}_1^*,\mathbf{a}_2^*,\mathbf{a}_3^*)$ to two dimensions. The average structure is a regular alternation of fat and skinny strips of rhombi, and is the projection of a regular three-dimensional staircase. Fluctuations around the average, the phasons, can be thought of as pushing a step vertically along $\mathbf{a}_2^*$ or horizontally along $\mathbf{a}_1^*$. The phason amplitude can be defined as the distance $x_\perp$ to the average structure. These fluctuations correspond to the fluctuations of the freedom line. Since the fluctuation of this line is uncorrelated, the mean square value $\bar{x}_\perp^2$ is proportional to the distance $X_\parallel$ from the origin, in good agreement with the experiments of Horn *et al.*[16] [$y=1$ in their formula (5)]. The length of fat or skinny strips of rhombi is described by the extension of the staircase along the $\mathbf{a}_3^*$ direction and is fixed by the boundary of the sector. This picture of random stacking of strips of fat and skinny rhombi has a diffraction pattern describable by the theory of Hendricks and Teller[13] and the tenfold symmetry of the diffraction pattern comes from the twenty orientations of the sectors.

The following properties are stated without proof: (i) All configurations without tears have the same energy for any given composition $B_c s_{1-c}$. (ii) In certain cases (for example, $W_s=1$ and $W_B=2$) this energy is the minimum energy, so that Fig. 2(b) represents one of many degenerate ground states.

Since this special case of $W_s=1$ and $W_B=2$ does not satisfy Eq. (3), our growth model generates structures with tears [Fig. 2(a)], implying that the state obtained is not the ground state. The concentration c does not appear in our dynamical model and cannot be easily introduced unless annealing is allowed at the surface of the growing cluster, as done by Elser.[12] Elser observed that more annealing decreases the anisotropy of the resulting structure, and this can indeed be expected in our model too. In the case of Fig. 2(b), each sector consists of randomly alternating strips of fat and skinny rhombi, with respective compositions B_2, s_2, and Bs_2. Therefore the average composition is $B_3 s_4$.

In conclusion, a very simple growth model has been studied. It generates structures with a high local anisotropy (i.e., a symmetry lower than tenfold) which appears clearly in Eq. (5). In addition, the structure is not quasiperiodic, but of the Hendricks-Teller type. Both properties (anisotropy and lack of quasiperiodicity) are observed experimentally, although to a much weaker extent than in our model. More realistic results could presum-

ably be obtained at the cost of complications of the model.[17]

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[17]An idea of the complication of real quasicrystals can be found (together with an up-to-date bibliography) in a review by C. L. Henley, to be published.