

# Kinetics of layer-by-layer growth and formation of the structure of icosahedral phases

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The layer-by-layer growth of an icosahedral quasicrystal from the melt is analyzed. The possibility of a congruent formation of a periodic crystal (with the approximant structure) is analyzed for various degrees of supercooling. The choice of mechanism for stabilizing the icosahedral phase (the mechanism involving the internal energy or the mechanism involving the entropy) predetermines the atomic structure which forms at a small degree of supercooling.

Fundamental structural features of quasicrystals are manifested in all related physical problems. In particular, in a study of the formation of these quasicrystals it becomes necessary to modify the conventional picture of a local growth of crystals, in which the probability for the attachment of an atom to a growing surface is determined through consideration of the interaction of this atom with only a small number of nearest neighbors.<sup>1</sup> Although various local-growth algorithms have been proposed,<sup>2</sup> it is generally believed that long-range correlations on the growing surface are necessary for the formation of a perfect quasicrystal.<sup>3</sup> Furthermore, the quasicrystal-melt boundary is thermodynamically smooth at any temperature.<sup>4,5</sup> Consequently, the quasicrystal grows by a layer-by-layer method if the degree of supercooling is sufficiently small.<sup>6</sup> This conclusion agrees with the faceting of the grains of stable quasicrystals which has been observed in several experiments.<sup>7,8</sup>

The kinetics of quasicrystal growth has been studied previously by numerical simulation<sup>9</sup> and by an analytic method in a continuum model.<sup>10</sup> The degrees of supercooling corresponding to the appearance of a kinetic roughness<sup>6</sup> of the growing face have been found. When this roughness appears, the growth rate switches from expo-

ponential to linear. In the present letter we analyze a microscopic model of layer-by-layer growth of a quasicrystal from the melt. We also examine the possible formation of a crystalline phase created by icosahedral structural elements: rhombohedra of two types.

In the layer-by-layer growth of an ordinary crystal, the interface between the liquid and solid phases moves as a result of a fluctuational formation of 2D nucleating regions and their subsequent expansion. In the course of this expansion, the atoms of the melt attach to steps on the plane boundary.<sup>1</sup> The critical radius and the critical energy of a nucleating region are

$$R_c = \frac{\alpha}{\Delta\mu}; \quad \text{and} \quad E_b = \frac{\pi\alpha^2 h}{\Delta\mu}, \quad (1)$$

respectively, where  $\Delta\mu = \mu_c - \mu_L$  is the supercooling per unit volume of the crystal ( $\mu_c$  and  $\mu_L$  are the chemical potentials of the liquid and the melt, respectively),  $h$  is the height of a nucleating region, and  $\alpha$  is the surface energy of the step front, which is introduced in a formal way in terms of the linear energy  $\epsilon_s$ :  $\alpha = \epsilon_s/h$ .

The structure of a quasicrystal can be thought of as a certain packing of rhombohedra of two types. The faces can be thought of as macroscopically plane surfaces which pass through the vertices of these rhombohedra and which are oriented normal to the wave vectors of the maxima on the diffraction pattern. Since these maxima fill reciprocal space densely, the height of a step is not fixed, while in a crystal it would be (it would be equal to the lattice constant). In the case at hand, the step height can take on values from a set of "interplanar distances" which fill the number axis.<sup>11</sup> The surface energies at the base and "roof" of the nucleating region are different, since the structure of a quasicrystal is not invariant under translations. The energy of the nucleating region thus acquires an additional component, proportional to the area of this region. An "effective supercooling" which depends on  $h$  should appear in expression (1) for the critical energy:

$$\Delta\mu_{eff}(h) = \Delta\mu - \Delta\sigma(h)/h, \quad (2)$$

where  $\Delta\mu = \mu_{QC} - \mu_L$  is the degree of supercooling of the melt with respect to the interior of the quasicrystal. The equilibrium shape of the nucleating region is thus determined by the possibility that not only the radius but also the height of this region will change.

In order to determine  $\Delta\sigma(h)$  we need to examine the change in the structure of a face of the quasicrystal upon a translation through a distance  $h$  in the direction normal to this face. In the method of projection from a six-dimensional space,<sup>12</sup> the positions of the quasicrystal atoms are specified by the orthogonal projection of the sites of a hypercubic lattice in a "tube" running parallel to the physical three-dimensional subspace. A translation corresponds to a displacement of this tube by the vector of the hypercubic lattice,  $\vec{H}$ , with an orthogonal component  $\vec{h}$ .<sup>1</sup> This vector takes some of the sites outside the tube, causing a redistribution of atoms on the surface under study. We would naturally relate the average difference between the energies of the face in the new and old positions with the fraction (or density) of atoms which change position. Up to a certain point, this approach is analogous to the method of ruptured bonds in

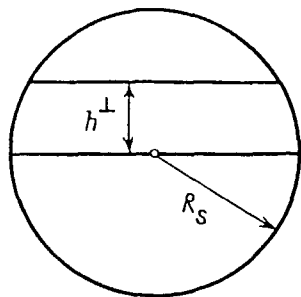


FIG. 1.

the problem of crystal faceting.<sup>1</sup> The smaller the value of  $h^\perp = |\vec{h}^\perp|$ , the smaller the change in the structure of the face as the result of the translation, and the smaller the difference in energies. As  $h^\perp \rightarrow 0$ , we find  $\Delta\sigma(h) = 0$ , as we should in a crystal.

If we approximate the cross section of the tube in six-dimensional space by a sphere of radius  $R_s$  (as is done in calculating diffraction intensities<sup>13</sup>), then the density of atoms which change position on the face of the quasicrystal upon a translation is related to the change in the areas of the corresponding two-dimensional cross sections of this sphere (Fig. 1) as follows, for small values of  $h^\perp$ :

$$\Delta n \propto (h^\perp/R_s)^2. \quad (3)$$

The change in surface energy is then  $\Delta\sigma \propto (h^\perp)^2$ , and the expression for the "effective supercooling" becomes

$$\Delta\mu_{eff}(h) = \Delta\mu - A \frac{(h^\perp)^2}{h}. \quad (4)$$

The values of the height  $h$  which are realized during the growth of the quasicrystal are predetermined by the positive sign of  $\Delta\mu_{eff}(h)$ , i.e., by the condition

$$h\Delta\mu > A(h^\perp)^2.$$

On the other hand, the height of a nucleating region which grows at a given bulk supercooling  $\Delta\mu$  corresponds to a minimum of the nucleation energy  $E_b$  in (1). In the expression for this energy, the supercooling  $\Delta\mu$  should be replaced by  $\Delta\mu_{eff}$ , found from (4). To some extent, this approach is analogous to determining the equilibrium shape of the nucleating region in the theory of the growth of ordinary crystals. We know that a minimization of  $h^\perp$  at a given  $h$  is achieved when  $\vec{H}$  is oriented along one of the six-dimensional vectors which generate the crystalline approximants of the quasicrystal,<sup>14</sup> for which the following expressions hold:

$$h_m^\perp = 2a_R\tau^{-m}(3-\tau)^{-1/2}; \quad h_m = 2a_R\tau^m(3-\tau)^{-1/2}. \quad (5)$$

Here  $\tau = (\sqrt{5} + 1)/2$  is the "golden section,"  $a_R$  is an edge of the elementary rhombohedron, and  $m$  numbers the approximants in order of increasing  $h_m$ . Substituting these relations into (4), we find the following expression for the growth of a quasicrystal:

$$\Delta\mu_{eff}^{QC} - \Delta\mu \propto \tau^{-3m} \quad (6)$$

Minimizing the critical energy  $E_b$  which we have found with respect to  $h$ , we can determine how the height of the nucleating region and the corresponding growth rate depend on the degree of supercooling:

$$h \propto (\Delta\mu)^{-1/3}; \quad v(\Delta\mu) \propto \exp(-C(\Delta\mu)^{-4/3}), \quad (7)$$

where  $C$  is a constant. These relations agree with the results found by Toner<sup>10</sup> in a study of a continuum model. Note that condition (7) implies that the height of the step diverges at a small degree of supercooling.

Since the structure of crystalline approximants is formed by the same elementary rhombohedra,<sup>15</sup> in each step of the growth of quasicrystal the formation of nucleating regions of the quasicrystal may be accompanied by a simultaneous formation of nucleating regions of approximants, whose height will be equal to the lattice constant of the crystal. If this lattice constant is the same as the thickness of the last filled layer of the quasicrystal, the structure of the surface at the base of the nucleating region of the approximant and that at its roof will be the same, and their energies will be equal. The ratio of the probabilities for the nucleation of a quasicrystal and of an approximant is thus determined by the difference  $\Delta\mu_{eff}^{QC}$  and by the bulk supercooling of the melt with respect to the approximant,  $\Delta\mu_{AP}$ . If  $\Delta\mu_{eff}^{QC} < \Delta\mu_{AP}$ , the nucleation of a crystal is more likely, and the crystal growth rate is higher (aside from a preexponential factor, which has approximately equal values because of the similarities in the structure of the quasicrystal and the approximant). In this case the layer-by-layer growth leads to the formation of a crystalline approximant. If  $\Delta\mu_{eff}^{QC} > \Delta\mu_{AP}$ , on the other hand, the growth rate will be higher for the quasicrystal.

The relation between the bulk free energies of the quasicrystal and of the crystalline approximants can be found in either of two models for the stabilization of icosahedral phases.<sup>16</sup> One of these models—the perfect-quasicrystal model—assumes that the minimization of the energy is achieved by virtue of a smaller internal energy of the quasicrystal. The difference is proportional to the number of atoms which occupy positions in the structure of the approximant which are different from those in the quasicrystal. In terms of the six-dimensional projection, this number is related to the relative number of sites of the hypercubic lattice which turn out to lie outside the tube when the tube is rotated from an icosahedral orientation.<sup>17</sup> It can be shown that this fraction is proportional to  $h^{-1}/h$ . Using (6), we then find the following relation for the degree of supercooling:

$$\Delta\mu_{AP} - \Delta\mu \propto \tau^{-2m} \quad (8)$$

In the random-packing model<sup>18</sup> it is assumed that the internal energy of the crystal is lower than that of the quasicrystal, which stabilizes above a certain temperature by virtue of a higher entropy. Analysis shows<sup>19</sup> that, upon a deviation of the tube in the six-dimensional space from an icosahedral position, the change in energy is proportional to the square of the phason deformation  $(h^{-1}/h)^2$ . For the degree of supercooling we then find the relation

$$\Delta\mu_{AP} - \Delta\mu \propto \tau^{-4m}. \quad (9)$$

These relations determine the structure which forms as the result of a layer-by-layer growth at small values of  $\Delta\mu$ , which correspond to large values of  $m$ . If the model of a perfect quasicrystal [relation (8)] is valid, then the inequality  $\Delta\mu_{\text{eff}}^{\text{QC}} > \Delta\mu_{AP}$ , becomes satisfied at a certain value of  $m$  and leads to the formation of a quasicrystal. If expression (9) (a random packing) is valid instead, then for values of  $\Delta\mu$  below a certain level we have  $\Delta\mu_{\text{eff}}^{\text{QC}} < \Delta\mu_{AP}$ , and the approximant grows at the higher rate.

In summary, by studying the growth of icosahedral quasicrystals at a low degree of supercooling one can test various models for the stabilization of these quasicrystals.

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