

# Growth kinetics of quasiperiodic structures at a low degree of supercooling

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The growth of a quasiperiodic structure at a low degree of supercooling  $\Delta\mu$  has been studied by the Monte Carlo method. The heights of the nucleating regions have a broad, discrete spectrum during the growth. The average height diverges as  $\Delta\mu^{-1/3}$ , in agreement with the results of analytic calculations. The growth kinetics is determined by the nucleating regions of greatest height. As a result, there are corresponding features on a plot of the growth rate versus the degree of supercooling.

A phenomenological model with a Hamiltonian corresponding to the sine-Gordon equation is widely used in research on the thermodynamics of crystal surfaces and on the kinetics of these surfaces during growth processes. This Hamiltonian is<sup>1,2</sup>

$$H(z) = \frac{1}{2} \int (K(\nabla z)^2 + V(z)) d^2\vec{r}, \quad (1)$$

where  $z(\vec{r})$  is the height of the surface above a reference plane, expressed as a function of the vector  $\vec{r}$  in this plane;  $K$  is the stiffness of the surface; and  $V(z)$  is the surface pinning potential. In the case of a periodic crystal, it is customary to use the expression

$$V(z) = -V_0 \cos\left(\frac{2\pi}{a}z\right), \quad (2)$$

where  $a$  is the lattice constant along the  $z$  direction. This model leads to expressions for the roughening temperature and for the corresponding correlation length. The critical degree of supercooling, which corresponds to that point in the dynamic roughening of the growing surface at which the layer-by-layer growth of the crystal converts into a normal growth,<sup>3</sup> is determined by comparing the radius of a critical nucleating region with the correlation length.

Research on the structure of quasicrystal surfaces has revealed<sup>4–6</sup> that the surface remains thermodynamically smooth at any temperature. The reason is that the height of an elementary step on the facet of a quasicrystal can be arbitrarily large, so the energy of the end of this step is not canceled by the configuration entropy.<sup>3</sup> As a result, an elementary step with a positive linear free energy is found at any temperature. The possible formation of nucleating regions of various heights on a facet of a quasicrystal also causes a substantial change in the growth kinetics of these nucleating regions.

In a study of the growth of quasicrystals at various degrees of supercooling, Toner<sup>7</sup> used model (1) with the pinning potential

$$V(z) = -V_G \left( \cos(Gz) + \cos\left(\frac{G}{\tau}z\right) \right), \quad (3)$$

where  $\tau = (\sqrt{5} + 1)/2$  is the golden section, and the vector  $G$  is determined by the intensification of  $V_G$  with increasing scale of the surface. He showed that in the case of layer-by-layer growth the height of a critical nucleating region of minimum energy diverges as  $h \propto \Delta\mu^{-1/3}$ , and the growth rate depends on the degree of supercooling in accordance with  $R(\Delta\mu) \propto \exp(-C\Delta\mu^{-4/3})$ . During the layer-by-layer growth of ordinary crystals, in contrast, the height of the nucleating region remains constant, equal to the lattice constant, and the dependence of the growth rate on the degree of supercooling is  $R(\Delta\mu) \propto \exp(-C\Delta\mu^{-1})$ . Actually, Toner studied the growth of a quasicrystal with a nucleating region of fixed height; the height depended on the degree of supercooling. However, it is shown below that, even if the degree of supercooling is constant, the nucleating regions will have a broad spectrum of heights, and this circumstance will be reflected in the growth kinetics.

In this letter we are reporting a Monte Carlo simulation of model (1) with the pinning potential

$$V(z) = -V_0 \left( \cos\left(\frac{2\pi}{a}z\right) + \cos\left(\frac{2\pi}{\tau a}z\right) \right). \quad (4)$$

The growth process is assumed to be sequential, by which we mean that nucleating regions cannot appear on a previous layer until this previous layer has been filled (this assumption corresponds to the assumption that the nucleating regions grow at a rate much higher than the rate at which they appear).

In the case of layer-by-layer growth of an ordinary crystal, the formation energy of a nucleating region of critical size is

$$E_b = \frac{\pi\alpha^2 h}{\Delta\mu}, \quad (5)$$

where  $\alpha$  is the surface energy of the front of a step, which is introduced formally in terms of the energy per unit length,  $\epsilon_S$ :  $\alpha = \epsilon_S/h$ . The primary distinction in the case of a quasicrystal is that the surface energy  $V$  is not invariant under translation over some characteristic distance along the  $z$  axis. Since the energy of the "base,"  $V(z_0)$ , and the energy of the "roof,"  $V(z_0 + h)$ , of the nucleating region are different, the energy of the nucleating region acquires an additional component, proportional to the areas. In addition, the quantity  $\Delta\mu$  is replaced in expression (5) for the critical energy by an effective supercooling  $\Delta\mu_{\text{eff}}$  which depends on the height of the nucleating region:

$$\Delta\mu_{\text{eff}}(h) = \Delta\mu - \Delta V(h)/h, \quad E_b = \frac{\pi\alpha^2 h}{\Delta\mu_{\text{eff}}(h)}. \quad (6)$$

The equilibrium shape of a nucleating region is thus determined by whether the height as well as the radius of this region can change. During the growth, there are evidently

nucleating regions whose height satisfies the condition  $\Delta\mu > \Delta V(h)/h$ , which gives a thermodynamic stimulus to the growth of these regions. The possible positions of the surface are described by the set of minima of the function  $V(z)$ . In the course of the simulation, the set of possible heights  $h$  of the nucleating regions was determined for each instantaneous position of the surface. For each such possible height, the probability for critical nucleation,  $\exp\{-E_b(h)/kT\}$ , was calculated. The height which was actually realized and the new position of the surface of the quasicrystal were then determined from random numbers. This process was repeated until the surface traveled a distance containing 8000 minima of the pinning potential. The simulation was carried out for degrees of supercooling in the interval 0.05–0.0002, in units of  $a\alpha^2/kT$ . The value of  $V_0$  was set equal to 1.

The distributions found for the heights which were realized are discrete for the degrees of supercooling studied. The observed heights correspond accurately to the sequence of Fibonacci numbers. Figure 1 shows distributions of the heights found for degrees of supercooling of 0.05 and 0.02. The changes in the spectrum of heights with the degree of supercooling are of two types. First (in a quasisteady regime), there is simply a redistribution of intensity among the three existing peaks in the spectrum. Second, there is a qualitative change, in the course of which a new peak, with a greater step height, appears in the spectrum. After the peak corresponding to the smallest height disappears, a quasisteady change in the spectrum occurs until the next critical degree of supercooling is reached. At this point, the spectrum shifts up the frequency scale. It is thus possible to introduce a set of critical degrees of supercooling  $\Delta\mu_c^i$ , at which nucleating regions with a height corresponding to the  $i$ th Fibonacci number appear.

The average height of a nucleating region,  $\bar{h}$ , increases with decreasing  $\Delta\mu$  (Fig. 2). The values found can be described accurately by the expression  $\bar{h} = \bar{h}_0 \Delta\mu^{-1/3}$ , where  $\bar{h}_0 = 9.1a$ . This expression was derived analytically by Toner.<sup>7</sup> Note, however, that the quantity  $\delta h$ , a measure of the dispersion of the height distribution, is a power-

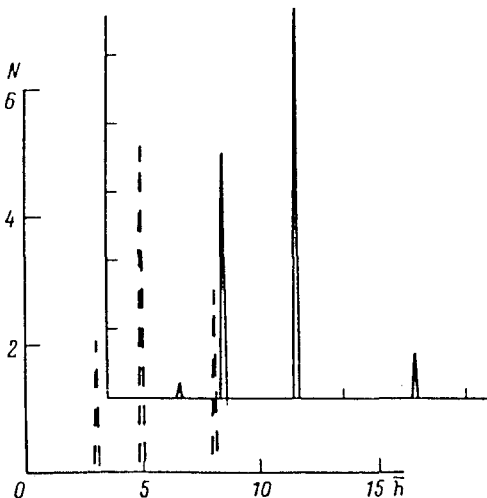


FIG. 1. Distribution of heights of the nucleation centers,  $N(h)$ , in arbitrary units. Dashed lines—For a degree of supercooling of 0.05; solid lines—0.02. The heights  $h$  are expressed in units of  $a$ .

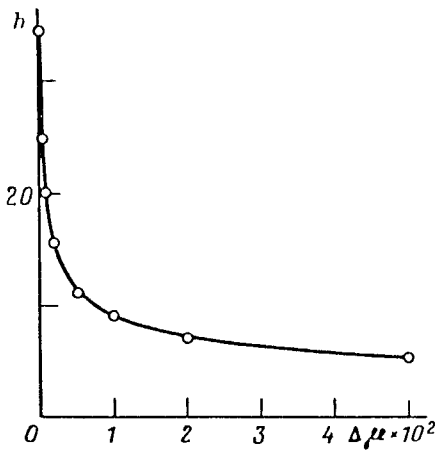


FIG. 2. Average height of a nucleation center versus the degree of supercooling. The solid line is a curve of  $\bar{h} = 9, 1a\Delta\mu^{-1/3}$ ; the circles are calculated values.

law function of the degree of supercooling, with the same exponent and with a coefficient  $\delta h_0 = 0.366$ . The average pinning energy realized during the motion of this surface is expressed as a function of the degree of supercooling by  $\bar{V} = -2 + 0.145\Delta\mu^{2/3}$ . We find the estimate  $\delta V = 4.095\Delta\mu^{2/3}$  for the measure of the dispersion of this energy.

In analyzing the growth kinetics we should bear in mind that, in the model of layer-by-layer growth which we are discussing here, the formation of nucleation centers with various heights occurs in succession, not simultaneously. The reason for the appearance of nucleation centers of greater height is that for certain positions of the surface the relief of the pinning potential is such that the formation of a nucleation center of lower height is impossible. The growth process is thus limited by the slowest steps. The time scale for the formation of a nucleation center is an exponential function of the critical nucleation energy, which in turn depends on the height of the nucleation center. Consequently, the formation times of nucleation centers with different heights are greatly different. Even at a supercooling of 0.05, the ratio of the formation times of nucleating regions with heights of 8 and 5 (Fig. 1) is on the order of  $10^2$  or  $10^3$ . At a smaller degree of supercooling (which corresponds to a greater difference between nearest heights in the spectrum), this ratio increases sharply. The growth kinetics is thus determined primarily by the nucleation centers with the greatest height ( $h_{\max}$ ) in the spectrum, even when the relative number of such centers is small. The formation time of nucleation centers with lesser heights can be ignored, and it can be assumed that after the formation of a nucleation center with  $h = h_{\max}$  the surface instantaneously jumps over the distance to the next position, where we must expect the appearance of the next layer, with a height  $h_{\max}$ .

To estimate the behavior of the growth rate  $R$  as a function of the degree of supercooling (Fig. 3), we will qualitatively analyze two characteristic cases. We first consider a special set of values of the degree of supercooling  $\Delta\mu^*$ , each corresponding to a quasisteady region of the plot of the height spectrum of the nucleation centers

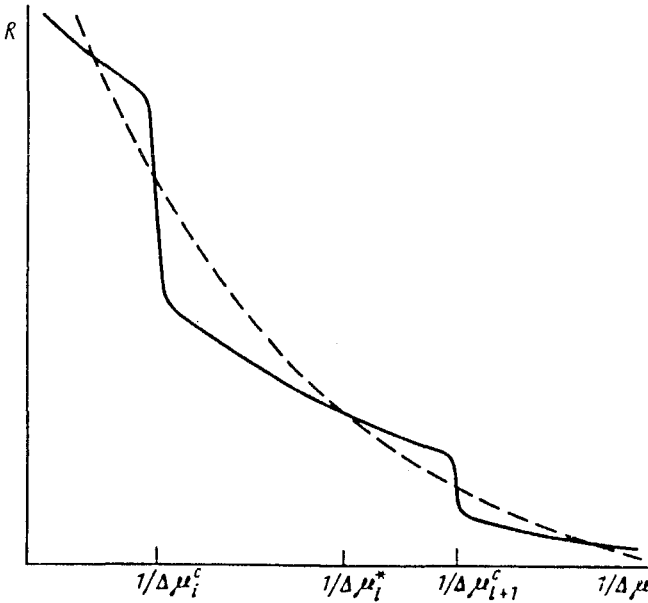


FIG. 3. Qualitative behavior of the growth rate  $R$  as a function of the degree of supercooling  $\Delta\mu$ .

versus the degree of supercooling ( $\Delta\mu_i^c > \Delta\mu_i^* > \Delta\mu_{i+1}^c$ ). The maximum height of the nucleation centers can be estimated from  $h_{\max}(\Delta\mu_i^*) = \bar{h}(\Delta\mu_i^*) + \delta h$ . At these points,  $R$  is proportional to  $\exp\{-\pi\alpha^2[\bar{h}(\Delta\mu_i^*) + \delta h]/(kT\Delta\mu_i^*)\} = \exp\{-\pi\alpha^2(\bar{h}_0 + \delta h_0)(\Delta\mu_i^*)^{-4/3}/kT\}$ ; i.e., the dependence is qualitatively the same as the  $R(\Delta\mu)$  dependence estimated for the average height of the nucleation centers. The only difference is in the coefficient of  $\Delta\mu$ . This dependence is shown by the dashed line in Fig. 3. As  $\Delta\mu$  varies from  $\Delta\mu_i^c$  to  $\Delta\mu_{i+1}^c$ , the height  $h_{\max}(\Delta\mu_i^*)$  of the nucleation centers which determine the growth kinetics does not change (as in a crystal). The growth rate is, within a preexponential factor which is a power function of  $\Delta\mu$ , proportional to  $\exp(-C\Delta\mu^{-1})$ . We now consider the vicinities of a critical degree of supercooling,  $\Delta\mu_i^c$ . In a narrow interval of  $\Delta\mu$ , nucleation centers with a new maximum height  $h_{\max}$ , corresponding to the next value of  $\Delta\mu_i^*$ , appear, and they begin to play a governing role in the kinetics. The growth rate thus decreases sharply in this interval of degrees of supercooling. The solid line in Fig. 3 shows the qualitative  $R(\Delta\mu)$  dependence. We see that incorporating the actual nature of the spectrum of the heights of the growing nucleation centers leads to fluctuations around the  $R(\Delta\mu) \propto \exp(-C\Delta\mu^{-4/3})$  curve.

In summary, this Monte Carlo simulation has shown that a broad, discrete spectrum of heights of nucleation centers is realized during the growth of a quasiperiodic structure. The average height diverges as  $\Delta\mu^{-1/3}$ , in accordance with the results of analytic calculations. The growth kinetics is determined by the nucleation centers with the maximum height. As a result, there are characteristic features on a plot of the growth rate versus the degree of supercooling.

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- <sup>1</sup>S. T. Chui and J. D. Weeks, *Phys. Rev. B* **14**, 4978 (1976).
- <sup>2</sup>P. Nozieres and F. Gallet, *J. Phys. (Paris)* **48**, 353 (1987).
- <sup>3</sup>A. A. Chernov, *Modern Crystallography, Vol. 3*, Nauka, Moscow, 1984.
- <sup>4</sup>A. Garg and D. Levine, *Phys. Rev. Lett.* **59**, 1683 (1987).
- <sup>5</sup>R. Lipowsky and C. L. Henley, *Phys. Rev. Lett.* **60**, 2394 (1988).
- <sup>6</sup>L. V. Mikheev, *Phys. Lett.* **132**, 137 (1988).
- <sup>7</sup>J. Toner, *Phys. Rev. B* **43**, 915 (1991)

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