Shape Selection of Kompeitoh

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We carried out experiments on the collective crystal growth of sucrose into a form of candy known as Kompeitoh. We examined the process for the selection of granule size and the number of spikes formed on the crystal surface. We found that the characteristic size of spikes was proportional to the size of granules in the steady-state regime, although the proportionality coefficient was dependent on conditions such as the initial shape of the crystals. A selection process of surface structure during the crystallization appears to have been caused by the distribution process of sucrose solution during the mixing of granules. In addition, a phenomenological model of surface growth based on the obtained experimental results is presented herein.

1. Introduction

Kompeitoh is a common type of Japanese candy made of sugar (sucrose) crystals that has been produced for centuries. Kompeitoh is traditionally produced by a standard method, which is described below. First, small seed granules, such as sesame seeds, are placed in a large rotating pan that is heated to an appropriate temperature and warm syrup is then added. Highly viscous syrup is distributed over the granules through the mixing process, and the sucrose crystallizes as the water evaporates from the surface of the syrup. Several days are required to obtain large sucrose crystals having a diameter of approximately one centimeter. Remarkably, several spike-like structures emerge autonomously during crystal growth. A number of scientific reports (mostly in Japanese) describing the characteristic shape of kompeitoh, as shown in Fig. 1, have been published.[1–7]

The growth process of kompeitoh has a few interesting characteristics that may differ from ordinary crystal growth in the liquid or vapor phase. Throughout growth, viscous sucrose solution (syrup) is supplied from outside so that the surface of the sucrose crystal is covered by a wetting layer. To consider the boundary conditions for the growing interface, we therefore may need to account for the fact that the fluid motion affects both heat and material transports on the crystal surface.

As another feature of this system, the mixing of granules with avalanches constantly occurs, while there also exists an approximately closest packed region beneath the flowing region. Therefore, we may not be able to assume the uniformity and steadiness of the environment surrounding the crystals, and the interactions among granules may play an important role.

From the viewpoint of the physics of pattern formation, some authors have suggested that the similarity between kompeitoh growth and diffusion-limited aggregation (DLA)[8,9] originates from the symmetry-breaking mechanism during crystallization.[3,5] However, as described above, simple diffusive transport and aggregation processes may not be appropriate to describe kompeitoh growth. For instance, in a pioneering study on kompeitoh, Fukushima[2] pointed out the existence of regular crystal shapes with definite numbers of spikes, typically 27 or 28, which could not be explained by a DLA-like growth model.

In dendritic crystal growth, the capillary length for the solid-liquid interface is typically on the order of nanometers, and resulting crystals correspondingly exhibit fine micrometer structures. In contrast, the characteristic spacing of spikes observed in kompeitoh becomes much larger than this length scale, and is typically on the order of millimeters. The simplified boundary conditions assumed in the study of ordinary dendritic crystals with the Gibbs–Thomson effect may not be sufficient to explain the morphology selection for kompeitoh. To explain the large-length-scale instability seen in icicle growth, a theory that takes into account for the heat transport through laminar water flow on an ice crystal surface has recently been proposed.[10–12] These studies suggest that the hydrodynamic effects of a thin liquid layer may change pattern selection markedly, although the growth process seems to be very different from that of the present subject.

In this paper, in an attempt to clarify the relevant physical process in this seemingly complex system, we report the experimental results for shape selection during the growth processes of kompeitoh. In the following section, we briefly describe the experimental procedures and important parameters. In §3, we summarize the results of these experiments. In §4, we present an interpretation of the growth process of kompeitoh on the basis of our experiments, followed by a phenomenological dynamical model of the wet interface.

2. Experimental Procedure

The crystal growth is performed in a cylindrical copper drum having a radius of 12 cm and a width of 12 cm. The axis along which the container rotates is tilted from approximately 0 to 5 deg from the horizontal plane to avoid the segregation of granules into different sizes. The container is heated from the bottom using an electrical heating device, and the temperature of the container can be changed using a current controller attached to the heater. A liquid sucrose solution is delivered from a reservoir into the container through a thin tube, and drops of the solution fall from the outlet of the tube located near the axle of rotation
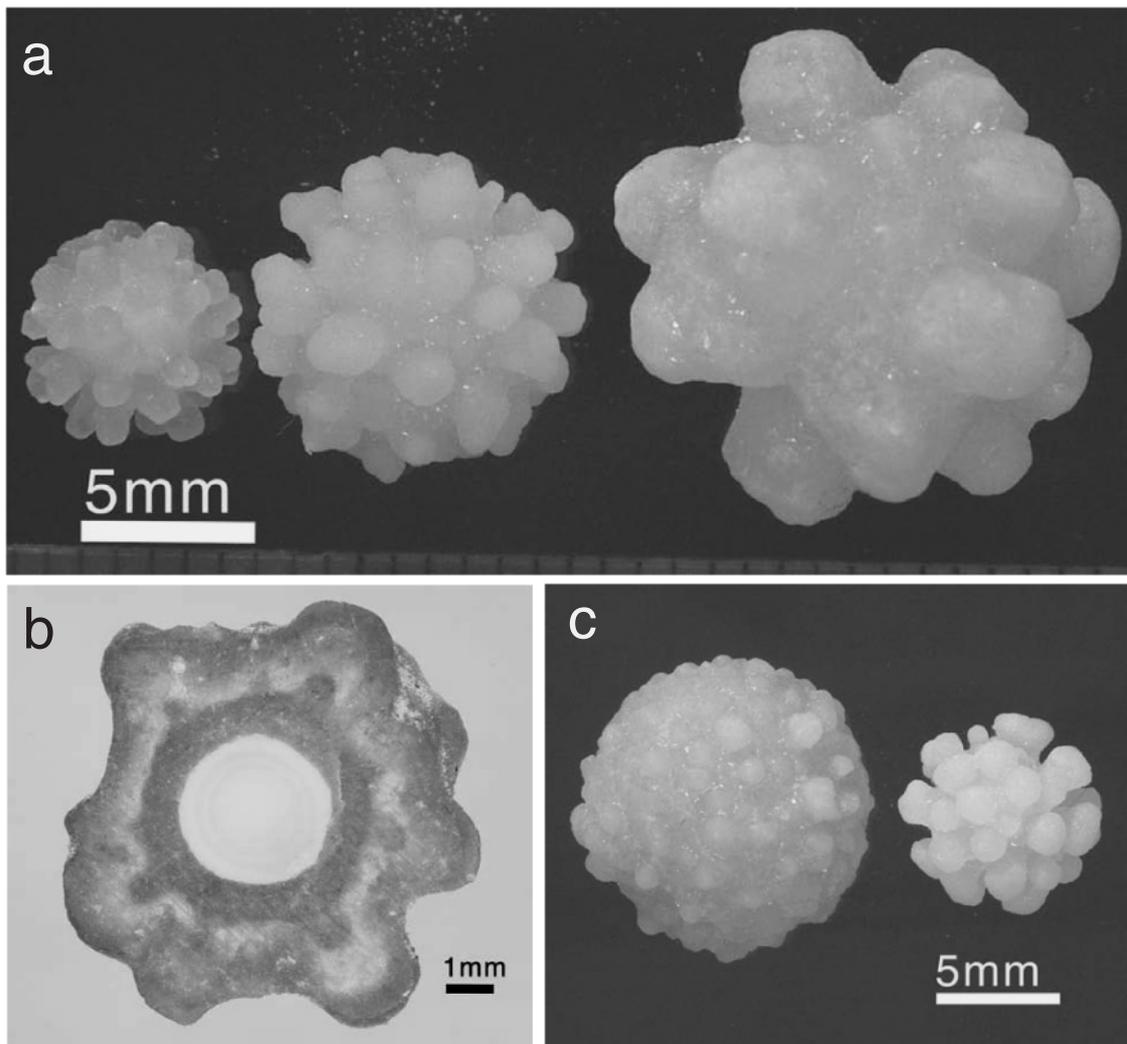
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Fig. 1. Samples of kompeitoh. (a) The growth times are 4, 10, and 18 h from left to right, respectively. (b) Cross section of kompeitoh. Sucrose solutions with/without dye were added alternately for 2 h. The white area at the center is the seed particle, which consists of tapioca starch. (c) Single larger seed particle (left) added to granules of smaller size (right). Samples are taken 4 h after the start of growth.

down to the spherical crystals. The flow rate can be controlled within the range from 10 to 500 cm^3/h.

The controllable parameters in our experiments are the flow rate of the sucrose aqueous solution Q (cm^3/h), the weight concentration of the solution C (g/cm^3), the temperature at the copper side wall of the container T ($^\circ$C), and the rotation speed of the container ω (rpm). The experiments are carried out at room temperature, $20 \pm 3\,^\circ$C.

The typical single time course of an experiment takes about 18 hours as described in the following:

(1) Place the seed granules in the rotating container and preheat them for approximately 30 min. In most cases, spheres of tapioca starch of approximately 3 mm diameter were used as the seed granules. The number of initial granules was approximately 1,500, which corresponds to a bulk volume of 40 cm^3. In addition, we tested various types and sizes of seed granules. Inside the rotating container, we observe a periodic avalanche of granules on the surface of the granular pile that occurs at intervals of approximately 1 s (for $\omega = 3$ rpm), which become shorter as ω increases.

(2) Start supplying the sucrose solution. At the very beginning, some of the seed granules stick together to form clusters. To avoid continued adhesion of these particles, we stir the particles with a rod during the first stage of growth. Thus, the resulting sucrose crystals contain only one seed granule.

Observations revealed that the surfaces of the sucrose crystals were covered by a layer of sucrose solution. Although the thickness of the layer could not be measured with the present experimental setup, the characteristic thickness was apparently less than sub-millimeters from visual observation. If the surface of the granules is dry owing to insufficient sucrose solution supply, the spherical shape remains stable and spike-like undulations are not observed. Since drops of syrup are supplied from a fixed position inside the container, only a very small number of granules near the top layer of the pile are subject to wetting at the same time.

To maintain constant the amount of sucrose solution supplied to the unit surface area on the granules, we increased the flow rate of the solution as a function of time t (min) according to the change in the total surface area. Otherwise, the surface conditions of the crystal may have changed drastically during the experiment.

The desirable condition is, therefore, $Q(t)/S(t) =$ const., where $S(t)$ is the total surface area of crystals. Since the total volume $V(t)$ of crystals increases as $dV/dt \sim Q(t)$, assuming a similar growth process $V \sim S^{3/2}$, $Q(t)$ needs to satisfy $Q^{1/2} dQ/dt \sim Q$. As the solution of this equation, we used the following quadratic form as the sucrose supply:

$$Q(t) = \alpha(t + \beta)^2, \tag{1}$$

where β is determined such that $\int_{-\beta}^{0} Q(t)\, dt$ is equal to the seed volume equivalent to the sucrose crystal volume, assuming perfect spherical growth. The typical growth speed of the surface was approximately 1 mm/h.

(3) During crystallization, periodic avalanches of particles occurred so that the particles collided and changed mutual positions. Depending on the number of seed particles and the growth rate, the total volume of the pile of sucrose crystals may exceed the limit of the container. In such cases, we remove some of the crystals to prevent the container from overflowing. In addition, we remove a small portion of the crystals for use as samples for measurement.

3. Experimental Results

The characteristic spike-like shape of kompeitoh is seen to be robust against the change in experimental parameters. Within the ranges of flow rates corresponding to $0.2 < \alpha < 2.4\ \text{cm}^3/\text{h}^3$ in eq. (1), container temperatures of $55 < T < 120\,°\text{C}$, and sucrose concentrations of $30 < C < 70\ \text{wt}\%$, we found that the initially rounded surface became unstable, allowing the formation of spikes. As a standard condition, we set the rotation speed of the drum to be $\omega = 3$ rpm.

If ω is small or zero, particles form clusters that consist of several seed particles. Consequently, without sufficient mixing due to the rotation, separated granules would not be formed. For $\omega > 3$, aggregation of crystal particles was not seen except in the very early growth stage. The rotation speed appears to affect the stability of the crystal surface as well. For $\omega = 3$ rpm, initial spikes were observed approximately one hour after the sugar solution supply was started. When ω was doubled (6 rpm), the first instability occurred after approximately 15 minutes. For larger ω, a portion of the granules remained spherical without spikes, and we eventually obtained inhomogeneous granular crystals having large deviations in size and shape. For $\omega > 4.5$, crystals segregated into different sizes in the container, and we found a broad distribution in diameter.

Figure 1(a) shows the typical shape of crystals at different growth stages. As discussed in the following, there is a tendency for the number of spikes to be reduced as the crystal grows. Figure 1(b) shows the cross section of a crystal formed over two hours that was alternatively colored with dye.

Figure 2 shows the distance between nearest spikes at the point when tiny spikes first appear. As seed particles, we used several types of approximately spherical objects, including beans. Note that the diameter of the granules plotted in the figure does not indicate the initial size of the seeds, but rather the diameter at which the instability is first seen. There is an apparent proportionality between the
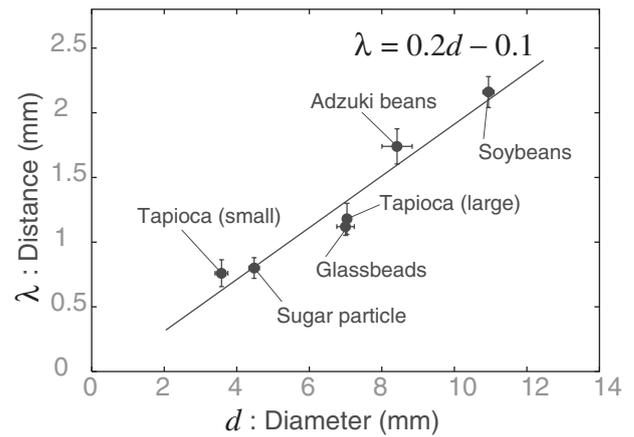

Fig. 2. Spacing of initially observed spikes for different sizes of seed particles.

diameter d and the selected interspike distance λ, and from fitting the data, we found that $\lambda \simeq 0.20d$. If we assume that the spherical surface is divided into equitriangles having vertices at the positions of the spikes, the number of triangles N_t required to cover a sphere of diameter d is estimated as $N_t \simeq 7.25(d/\lambda)^2$. When each vertex is shared by an average of six triangles, the number of spikes N_s is given by $N_s = 3N_t/6$. Using this formula, our estimation of the initial number of spikes is approximately 90, which is much larger than that observed in the later stage of growth.

Figure 3 shows the distribution function of N_s for the randomly sampled crystals at different times. The number of spikes constantly decreases to a certain number, and the distribution becomes sharper with growth. This is the general tendency for spherical seeds other than sucrose single-crystal of cuboidal shape. As shown in Fig. 4, the size distribution also narrows at the same time.

Although sharpening of the distribution is clear, the number of spikes that eventually form may change depending on the experimental conditions. In addition to 24 spikes, we also observed the 20-spike case, as shown in the inset of Fig. 3. Furthermore, for the case of starting from a sucrose single crystal, which is common for commercially available
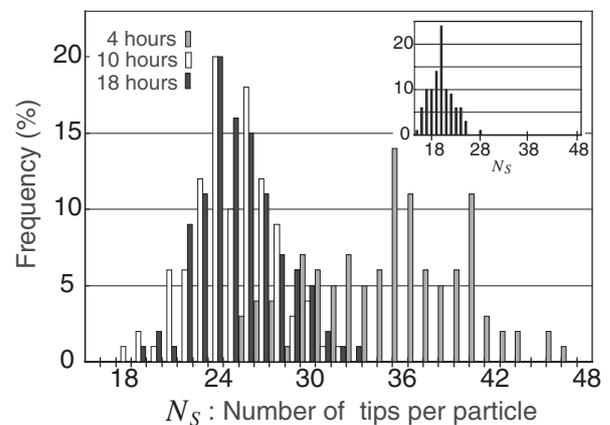

Fig. 3. Distribution of number of spikes during different growth stages (4, 10, and 18 h). The inset shows the plot for the same experimental conditions at 18 hours, which has a different peak position (20). More than 100 samples were used to make these plots.
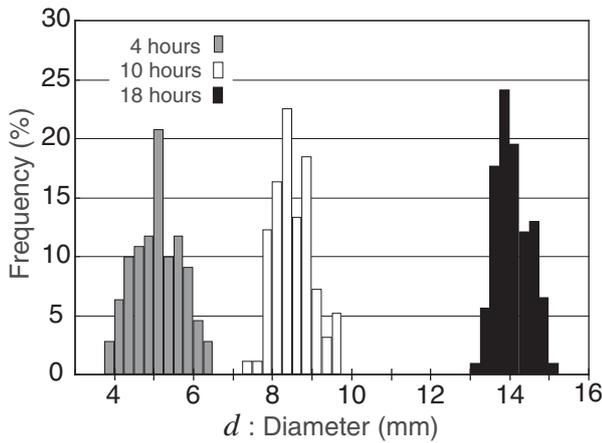
Fig. 4. Distribution of tip-to-tip diameter of samples for data shown in Fig. 3.
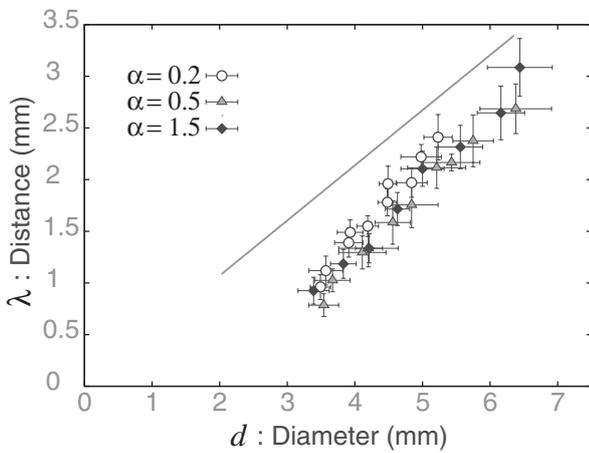

Fig. 5. Tip-to-tip distances λ of spikes with respect to crystal diameter d during growth starting from seeds of 3 mm diameter. Data for different flow rates of sucrose solution are plotted in the same plane. The solid line represents the λ–d relation for the case in which each spike is located at the vertex of the dodecahedron.

kompeitoh candy, the selected number becomes smaller than 20.[6] These numbers are significantly smaller than those reported in ref. 2.

In Fig. 5, we plot the interspike distance during growth for different flow rates of sucrose solution. In the plot, the data for the very early growth stage are excluded. The flow rate Q has only a minor effect on the shape selection process. Since the flow rate exhibits an asymptotically linear relationship with diameter, from the overall slope of the plots, we can estimate that an average of 20 spikes will be selected by comparison with the intervertex distance versus diameter relation of dodecahedron with 20 vertices (solid line in Fig. 5).

To measure the crystal size and irregularity, it is convenient to introduce two crystal diameters: the first diameter is that of a circumscribed sphere of the crystal, d_1, and the second diameter is that of the "inner" base sphere upon which spikes are formed, d_2. On the basis of the measurement of commercially available samples, Fukushima claimed that there is a steady-state growth regime in which the ratio of the radii of the two spheres,

d_2/d_1, is maintained constant at approximately 0.8.[2] We also confirmed that this ratio becomes constant during the later stage of growth. However, the measured value of the ratio in the present experiments was approximately 0.6, which appears to be significantly smaller. This discrepancy may have arisen owing to insufficient growth of the crystals used in ref. 2 to discuss a "self-similar" region in which the shape and number of spikes are selected.

4. Discussion

4.1 Growth process

In our experiments, we could not find a "magic number" of spikes to be finally selected. In contrast, the selected number of spikes appears to be affected by subtle changes in the experimental conditions. However, there is an evident tendency in the selection process of the number of spikes, as long as the conditions are such that near monodispersity of the granules is maintained (Figs. 3 and 4). That is, the initial broad distribution is focused into a single peak through growth. Therefore, we expect that the interaction of granules during crystal growth is crucial to spike formation and that the number and spacing of spikes are determined collectively through the growth.

In support of this theory, we observed that a similar corrugated surface of sucrose crystals with spikes was also deposited on the cylindrical wall of the container when the sucrose drops happened to condense on the hot surface. The spacing of the spikes became identical to that of the granular crystals inside.

Furthermore, we intentionally added single particles of larger diameter to the granules of standard size. Spikes formed on the larger seeds in a manner such that the spacing of the spikes was "duplicated" as a result of smaller granules surrounding the larger seeds [see the photograph in Fig. 1(c)], although the spacing of the spikes was proportional to the particle diameter if the process was started from monodispersed granules, as shown in Fig. 2.

From the above observations, the kompeitoh growth process is described as follows:

(1) At the very early stage, instability first occurs due to the crystallization of the sucrose solution that is delivered onto the surface by contact processes. Since the distance between initial spikes is proportional to the diameter of the granules (Fig. 2), the contact process and/or packing of granules, rather than intrinsic instability mechanisms of crystal growth, such as the Mullins–Sekerka instability, is influential on the unstable wavelength.

(2) The protruding surface has a greater chance of acquiring sucrose solution from other granules so that the growth of such parts is accelerated. It is thought that the instability is also promoted by a higher evaporation rate of water at the convex superior region. On the other hand, the tips of the spikes also have a greater chance to provide solution to other granules. It is very likely that the exchange of fluid takes place simultaneously at more than one contact point because the granules are densely packed. As a consequence, spatial correlation of the crystal surface is also transferred during the contact process, which will bring about an autocatalytic effect, exhib-

iting the focusing effect mentioned in the previous section.

(3) During crystal growth accompanied by mixing, the distance between spikes, as well as the diameter of particles, is regulated. There is a tendency for the number of the spikes to decrease gradually. After the transient growth stage, the system enters a self-similar growth regime, where the shape of crystals remains the same and the number of spikes has a sharp single distribution.

In a diffusion-limited growth process with some stabilizing effects, the stability of the moving interface is expected to depend on the growth speed.[13,14] On the other hand, on the basis of Fig. 5, the characteristic length scale to be selected is independent of the average growth rate of the interface, which is proportional to the flow rate Q. We therefore conclude that, at least, for the selection of the spike pattern, the transport of heat and vapor is not the governing process.

Kametani and Yamauchi reported the appearance of crystals similar to kompeitoh during the electrodeposition of nickel in a vibrating bed cell using a suspension electrolysis technique.[15] Despite the differences in the material properties and growth mechanism, they obtained very similar metal objects, typically having 28 to 30 spikes. This may not be a coincidence if the interaction of granules is crucial to pattern formation.

4.2 Phenomenological model of wet surface growth

Next, we consider the phenomenological model for the surface growth in terms of the interface equation of motion based on the above discussions. Upon contact a wet granule, a portion of viscous liquid is delivered near the contact point. Since the concentration of the solution is chosen to be near saturation, crystallization can occur quickly, upon water evaporation from the interface. From conservation of sucrose, if the wetting layer is sufficiently thin, the underlying solid–liquid interface will follow the liquid–vapor interface.

During the condensation, we can expect the fluid motion to be driven by surface tension. Imagine that the surface of the sucrose crystal is covered by an added wetting layer of characteristic thickness w, the initial shape of which is given by an adhesion and peering process of liquid during mixing. For the case in which w is small and changes very slowly in space, the local pressure P is determined by the Laplace law as

$$P - P_0 = \sigma H, \tag{2}$$

where H is the mean curvature of the liquid–vapor interface, P_0 is the constant atmospheric pressure, and σ is the surface tension of the interface.

On the solid–liquid interface, the nonslip boundary condition is appropriate, whereas the liquid–vapor boundary is stress-free. Therefore, if the change in w is sufficiently small, by solving the Navier–Stokes equation for the high-viscosity limit, the velocity, u, for uniform flow along the interface becomes

$$u = \frac{\sigma}{\eta} \nabla H \left(\frac{z^2}{2} - wz \right), \tag{3}$$

where η is the viscosity. Taking the average in the z-direction, the fluid motion along the interface is described by

$$\bar{u} = \frac{1}{w} \int_0^w u(z) \, \mathrm{d}z = -\frac{w^2 \sigma}{3\eta} \nabla H. \tag{4}$$

For simplicity, let us consider the growth of the wet planar surface with small amplitude undulation. From the conservation of fluid, the height h of the liquid-vapor interface obeys $\partial h / \partial t + \nabla \cdot (w\bar{u}) = 0$. Using the above expression of $\bar{u}$,

$$\frac{\partial h}{\partial t} = -\frac{w^3 \sigma}{3\eta} \nabla^2 H, \tag{5}$$

where $H \simeq -\nabla^2 h$ in the leading order. This is similar to the surface diffusion for microscopic dynamics on solids at finite temperature.

It is plausible to assume that extruding a portion of the surface into vapor provides a larger growth rate. One reason for this is an excluded volume effect caused by finite-sized sucrose crystals. When the growing interface is surround by spherical crystals of diameter a, one can virtually draw an effective surface extended by the thickness a. If the granules distribute uniformly on the effective surface, the probability of occurrence of the contact process between a perimeter site and the crystals increases by a factor of $[(R_1 + a)(R_2 + a)]/(R_1 R_2) \simeq 1 + a(R_1 + R_2)/(R_1 R_2) = 1 + 2aH$, where R_x is the radius of curvature in the principal direction at the perimeter, as long as $a \ll R_x$. Thus, if crystallization is limited owing to the supplement of solution through collisions, the growth velocity of the curved interface having mean curvature H is modified by the factor $2v_0 aH$, where v_0 is the velocity of the interface. Even in the case of $a \simeq R_x$, this tendency remains, and the lowest relevant term has the same form as $c_2 H$, where c_2 is a constant that is proportional to v_0. In general, we can assume $c_2 = v_0 \xi$ using a characteristic length ξ, which depends on the origin of the instability.

Another possible reason for the instability of the curved front is the flux nonuniformity of the water evaporation process on an irregular surface, which causes "Laplacian instability". For small-amplitude surface fluctuations, this can be also represented in the form $c_2 H$, although the derivation of the explicit form of c_2 may not be straightforward.

Summarizing the above arguments with the first nonlinear correction term for an inclined surface with average growth velocity, the height h of the growing surface in the average growth direction will obey the following:

$$\frac{\partial h}{\partial t} = -c_2 \nabla^2 h - c_4 \nabla^4 h + g \left(1 + \frac{1}{2}(\nabla h)^2 \right) + F, \tag{6}$$

where $c_2 = v_0 \xi$, $c_4 = w^3 \sigma / 3\eta$, $g = v_0$, and F represent the exchange of sucrose solution, which is dependent on space and time. This equation is simply the Kuramoto–Sivashinsky (KS) equation[16] with an external forcing term.

In the study of the microscopic surface growth, Cuerno et al.[17] introduced a KS model with a random noise term and found a crossover from a periodic surface structure to an irregular surface structure. For the case of kompeitoh, F should have correlation in space according to the shape and packing structure of the granules that deliver the liquid. We

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need to derive a self-consistent formula that includes the liquid exchange process in conjunction with eq. (6). This is a topic for future study. Since the KS equation has a broad dispersion relation for long wavelengths, collective forcing around a wavelength may cause reinforcement and focusing, which leads to the selection of spikes other than those at the most unstable intrinsic mode. As a preliminary study, in the one-dimensional case, we carried out computer simulations of eq. (6) with a sinusoidal modulation $F(x, t) = \epsilon \sin(k_0 x + \phi(t))$, where $\phi(t)$ is a temporally independent noise in the phase and ϵ is a small number. We found that k_0, rather than the intrinsic unstable mode $k^* = (c_2/2c_4)^{1/2}$, is finally selected after a transient time. We expect that this *softly* unstable nature of the wetting interface is intrinsically important for shape selection through an adhesion and peeling cycle of sucrose solution accompanied by deposition.

Acknowledgment

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