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Oscillatory growth of dendritic tips in a three-dimensional system

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We report the observation of the coexistence of oscillatory-type and ordinary steady-type dendrites growing simultaneously from a seed, respectively, in the [111] and [100] directions in an undercooled succinonitrile-acetone solution. It is suggested that a kinetic effect may be responsible for the mechanism of oscillatory growth. The present observation may help in understanding the mechanism for oscillatory growth when the direction of growth is not along the principal axis of anisotropy of the surface tension.

The pattern selection of growing objects in nonlinear systems far from equilibrium has attracted many researchers.[1] Particularly, well-defined problems, such as the selection of the tip radius and the growth speed of the freely growing needlelike dendrite, have been studied both analytically and numerically with several definite results.[2] According to the present understanding of the selection mechanism of the tip, introduction of an anisotropic surface tension splits the continuous band of the Ivantsov solution into infinite discrete modes among which the fastest mode is linearly stable and the others are unstable against tip-splitting perturbation, if the growth direction of the tip is in the preferred orientation. In this theoretical scheme, which takes the anisotropy of surface tension into account, a needle tip growing in the principal axis of surface-tension anisotropy is stable.

Stability theory, however, does not exclude a possibility of the existence of oscillatory growth of finite amplitude. In fact, there have been a few reports in the past on the observation of oscillatory growth. Morris and Winegard[3] reported a pulsating tip growth in succinonitrile-5% camphor solution. It was only a brief report in which neither the condition for the observation nor the nature of oscillation was clarified. Honjo, Ohta, and Sawada[4] reported a pulsating type of growth in a two-dimensional system. Rolley[5] observed a similar type of growth in ^{3}He. The present work was undertaken to revisit the phenomena of oscillatory growth in three dimensions and examine its nature in the light of present stability theory on steady tip growth.

Succinonitrile with 8.1% acetone was confined in a flow cell of $35\times5\times1$ mm^3 immersed in a water jacket with view windows in the top and bottom sides for microscope observation. The temperature of the cell and the water jacket were independently controlled within an accuracy of 20 mK. The cell was first undercooled to 16 °C, letting many seeds be nucleated. Then all the seeds except for the one that is symmetric in the plane of observation were removed from the cell by use of forced flow in the cell. The cell containing one symmetric seed was annealed overnight at 19.5 °C, the equilibrium temperature. The shape of the seed becomes nearly spherical by annealing, still keeping the symmetric orientation in the cell. The vertical orientation of the seed in the present experiments was [110].

The temperature of the cell was then gradually lowered. The seed grew almost spherically until the temperature was lowered to 16.6 °C, the critical temperature for the Mullin-Sekkerka (MS) instability for the size of the present seed, when three small protrusions equally spaced on the surface nearly perpendicular to the [100] direction and two fatter protrusions on the boundary perpendicular to the [111] directions appeared [Fig. 1(a)].

Figure 1(b) shows coexistence of two growth forms different from each other: a dendrite growing in the [100] direction and one growing in the [111] direction. The former is the ordinary type of steady growth where the tip has a constant curvature and grows with a fixed speed. On the other hand, the latter manifested an oscillatory growth. In the oscillatory type of growth, the growth tip became gradually flattened [Fig. 1(c)] and then a new protrusion appeared at the center of the flat tip [Fig. 1(d)]. The protrusion became quickly pointed, and thereby the speed of the tip increased at this phase. Then, the flattening of the tip takes place again, and the processes of protruding and flattening are repeated by turns. The features are almost identical to the ones previously reported.[3] The important difference, however, in the present work is the coexistence of the oscillating type of growth and the ordinary steady type of growth.

Figure 2 shows the measured radius of curvature and the measured tip position as a function of time for the oscillatory dendrite growing in [111] at $T=16.6$ °C. They are normalized by the radius of curvature of the dendritic tip simultaneously growing in the [100] direction. It is worth noting that the radius of curvature in the oscillatory tip is smaller at its minimum than that of the steady tip. The period of protruding phase is about one-half of the flattening phase, and the growth speed of the tip at the producing period is about three times greater than

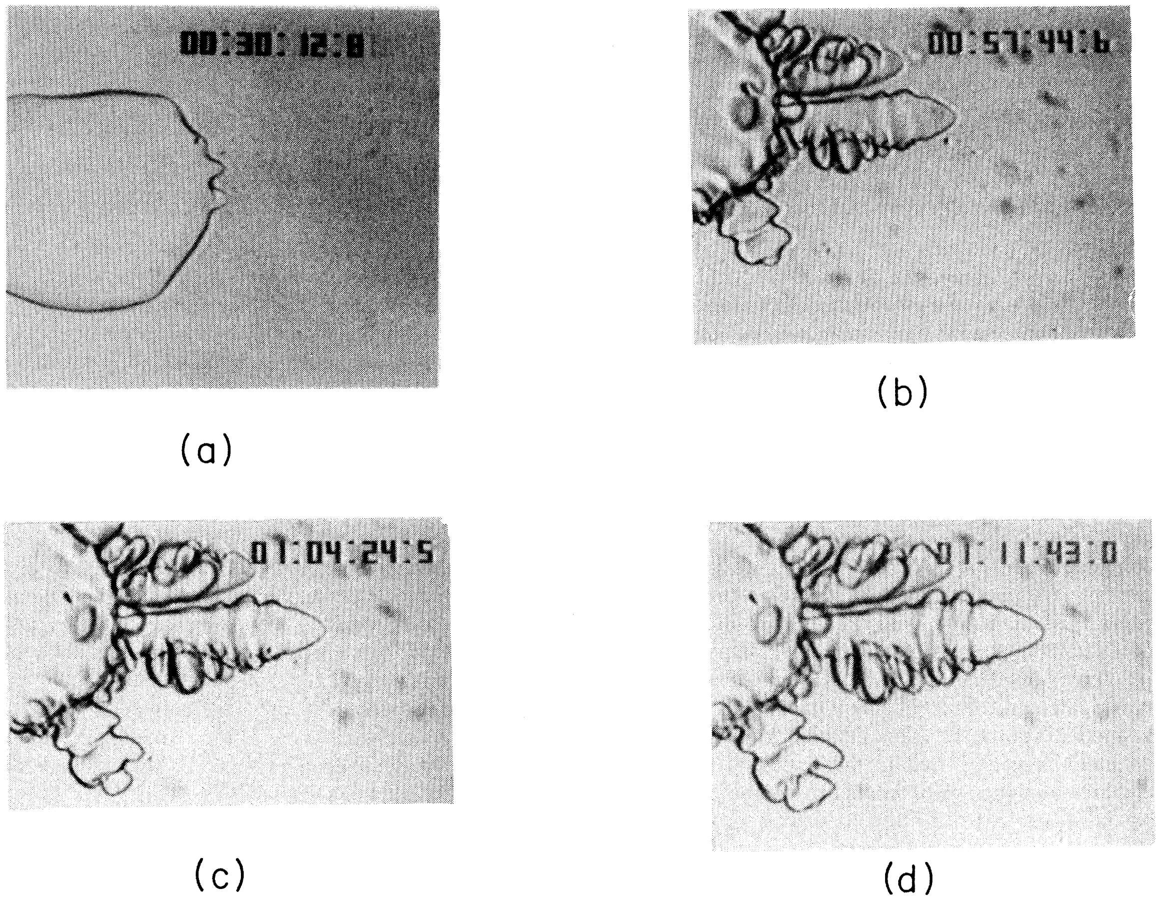

FIG. 1. (a) Beginning of budding after Mullin-Sekkerka instability of growing interface. The plane of figure is [100]. Three small buds pointing towards the right in the figure are growing in the [100] direction. Two fatter protrusions are seen in the downward and upward about 60° off from the [100] direction. They are to grow in the [111] directions. (b) Coexistence of an ordinary type of dendrite growing in the [100] direction and an oscillatory type of dendrite growing in the [111] direction at its third protruding period. (c) The oscillatory type of dendrite is at its third flattening period. (d) The oscillatory type of dendrite is at the beginning of the fourth protruding period.

the flattening period. Therefore, the flattening process is speed limiting for the oscillatory growth.

Figure 3 shows the dependence of the oscillation period on the degree of undercooling. The period sharply drops with increasing undercooling. If one assumes a power-law dependence, the critical temperature would be in the neighborhood of MS instability points (undercooling temperature equal to 2.4 °C or Δ equal to 0.065 in Fig. 3), clearly not in the neighborhood of the equilibrium temperature. If a MS instability point is chosen, for example, as the critical point, the critical exponent is 2.5 ± 0.4.

It was observed that the oscillatory growth has a protruding phase and a flattening phase. The former process is probably a MS instability of a flattened growing face, as the shape and the evolution look similar to the one observed initially on the flat surface. Since the MS stability is a linear instability, it can take place on a surface of any direction, even if it is not crystallographically the most preferred orientation. As the protrusion grows, the foot of the protruding surface turns gradually off the original orientation. If the original orientation is [111], as it is for the present case, the foot of the protrusion gradually faces a direction, such as the [100] direction, that is more preferred than the original one. Then it is expected that the part facing the more preferred orientation grows faster than the inferior direction. This process would flatten the protrusion. Then there are two choices. If the anisotropy of surface tension is large, the tip splitting would take place. If it is not very large, the flattening process would continue, and thereby the flat area facing the original orientation would increase, until the flat area becomes the order of the stability length for MS instability, when a protrusion would sprout again.

In the present case the average speed of the oscillating tip is about half the steadily growing tip [100] direction, but the growth speed of the protrusion in the [111] direction at its maximum is six times greater than the average growth speed of the oscillation tip, or three times greater than the stationary speed of a growing tip in the [100] direction. The fast growth speed of the protrusion at its birth is the first necessary requirement for avoiding tip splitting, and the slowing down of the protrusion at the next stage is the second requirement for the flattening.

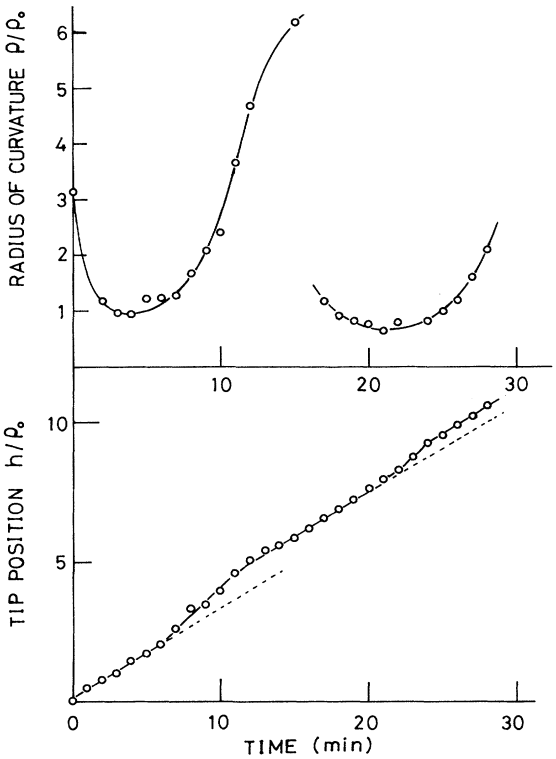

FIG. 2. The radius of curvature and the relative position of the tip as the function of time. They are normalized by the radius of curvature of the steady dendrite growing in the [100] direction.

An open question is, therefore, what interfacial dynamics is governing to satisfy these requirements.

The effect of the kinetic term in the boundary condition has been recently studied theoretically.[6,7] According to the linear stability analysis[6] of steady-state needle crystals by the boundary layer model, the steady-state needle crystals are linearly unstable, resulting in tip splitting or side branching for certain parameter regions in the presence of anisotropies in both surface tension and interfacial kinetics which have angular dependence different from each other. It is theoretically expected that the direction that favors the anisotropy due to the kinetic term is generally chosen when the growth speed is fast, while the direction that favors the anisotropy due to surface tension is chosen when the growth speed is slow. There may exist a parameter region of supercooling, in which the [111] direction and the [100] direction are almost equally favored as the growth direction. The physical mechanism of the oscillatory growth in the present work may be related to the competition between the surface-tension effect and the kinetic effect. The experimental results are consistent with the general expectation. Satisfaction of the first requirement may be attributed to the kinetic effect and that for the second requirement may be due to the surface-tension effect, not vice versa. Thus it is also consistent with the fact that the oscillatory growth is not experimentally observed in the surface-tension-favored direction A direct measurement of angular dependence of kinetic effects is necessary to clarify these points.

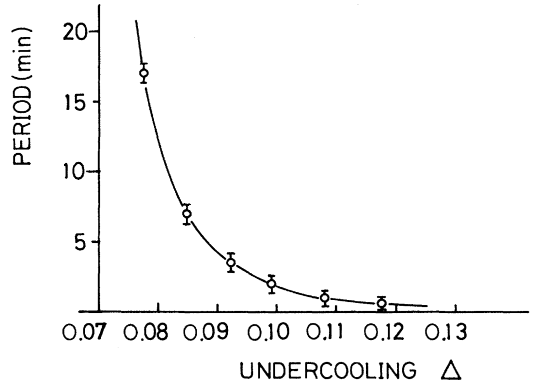

FIG. 3. The period of oscillation of the oscillatory growth in the [111] direction as a function of undercooling. The undercooling was calculated from the undercooling temperature and known liquidus line for the present solution.

Let us consider how these two stages take turns one after the another. The dependence of the period of oscillation was found to be controlled by the flattening process. If the speed of flattening is proportional to the growth speed of the surface-tension-preferred orientation, and if this speed has the same dependence on the undercooling with the steadily growing tip in the [100] direction, then the frequency should be inversely proportional to quadratic power of the undercooling, neglecting the weak logarithmic dependence. In this case the critical temperature for the initiation of oscillation would be the equilibrium temperature. The experimental results are not consistent with this viewpoint.

If the observed oscillatory growth is originated from a Hopf type of instability,[6] there should be a critical undercooling, at which the amplitude of oscillation vanishes but the frequency is finite. The present observation suggested that the frequency changes in a power law of the deviation from a threshold value of the undercooling for which the frequency vanishes. The observed strong dependence of the frequency on undercooling is not consistent with a Hopf-type instability. A more detailed study of critical behavior, if any, would be important.

Coexistence of two kinds of growth form in a solution is worth noting. It is remarkable to observe simultaneously two totally different growth mechanisms in a wide range of control parameters, which are selected only by the growth direction. The oscillatory growth pattern reported in the present work has a close resemblance to the one observed previously in a thin layer of aqueous solution of NH_4Cl confined between two glass plates.[4] The present results suggest that the oscillatory growth in the two-dimensional case may also be attributed to the competition between the kinetic effect and the surface-tension effect.

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[1]For example, see J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980); P. Pelce, *Dynamics of Curved Fronts* (Academic, New York, 1988).

[2]For a recent review, see, for example, D. Kessler, J. Koplik, and H. Levine, Adv. Phys. **37**, 255 (1988).

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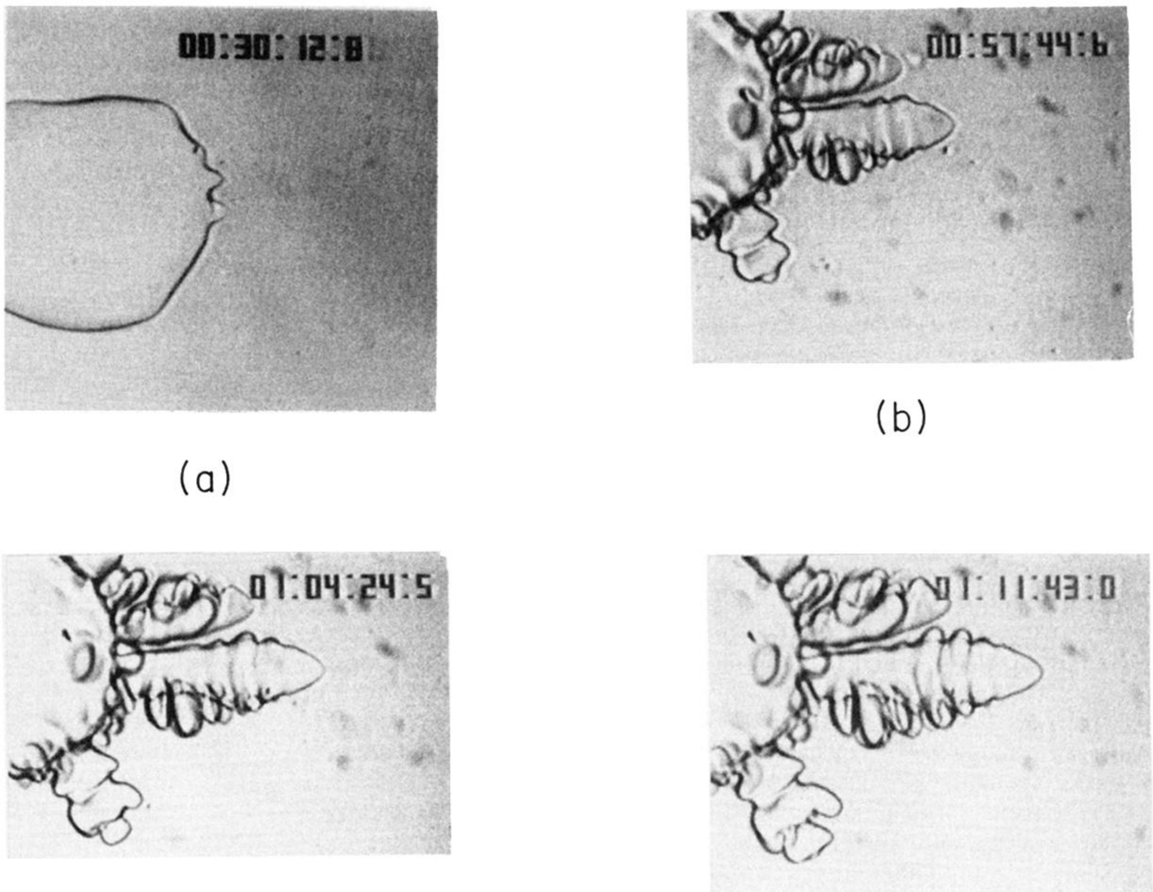

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