Spontaneous oscillatory phenomenon in crystal growth, accompanied by accelerated growth rate

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Mathematical aspect for interfaces and free boundaries
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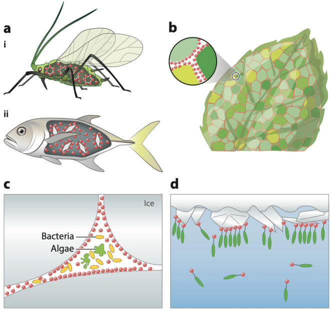
Ice-binding proteins (IBPs)



IBPs with anti-freeze effect (anti-freeze proteins, AFPs)[1]

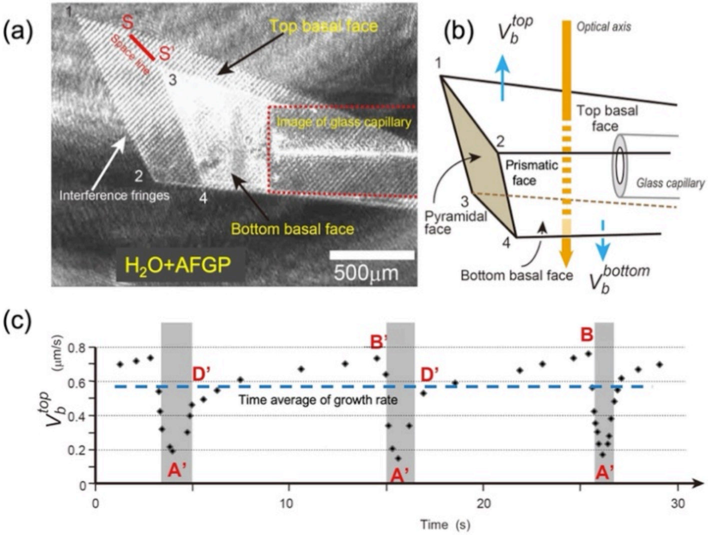
AFPs adsorb on ice-crystal surface and inhibit its growth, but the mechanism is still unsolved.

Ice-crystal growth in supercooled water including AFGP8[2] was observed in ISS.[3] It was found that the growth rate oscillates periodically, despite the constant supercooling setting (spontaneous oscillatory growth).

[1] M. Bar Dolev et al. (2016), *Ann. Rev. Biochem.* **85**, 515.

[2] Antifreeze glycoprotein 8. A type of AFP.

[3] Furukawa et al. (2021), *Int. J. Microgravity Sci. Appl.* **38**, 380101


(a)
S
S'
Space line
Top basal face
1
3
Image of glass capillary
2
Interference fringes
4
Bottom basal face
H_2O+AFGP
500μm
(b)
V_b^{top}
Optical axis
1
Top basal face
2
Prismatic face
Glass capillary
3
Pyramidal face
4
Bottom basal face
V_b^{bottom}
(c)
V_b^{top} (μm/s)
0.8
0.6
0.4
0.2
0
B'
B
D'
D'
A'
A'
A'
Time average of growth rate
0
10
20
30
Time (s)

Why does oscillation occur?

As ice grows, latent heat of crystallization is released, which rises ambient water temperature, decreases supercoolin, and then suppresses ice-crystal growth.

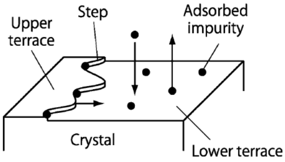
However, the release of latent heat alone does not induce oscillation. As the growth rate decreases, the release of latent heat also decreases, and the system settles to a steady state in balance with the dissipation of latent heat.

Possible answer

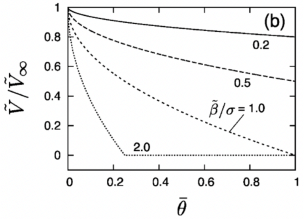
Positive feedback between

1. Impurity inhibits crystal growth
2. Crystal growth keeps the surface clean

Impurity inhibits crystal growth



Terrace and step on crystal surface



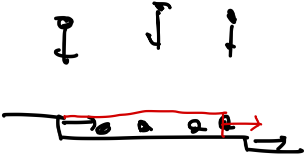
Molecules are incorporated at step edge, step goes ahead, the surface builds up layer by layer.

Adsorbed impurities inhibit step motion. The higher the density ($\bar{\theta}$), the smaller the step velocity ($\tilde{V}$).[4]

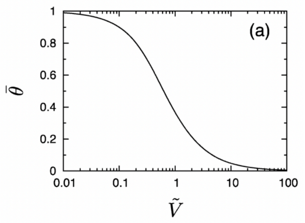
$$\tilde{V}/\tilde{V}_\infty = 1 - \tilde{\beta}\bar{\theta}^{1/2}/\sigma \qquad (1)$$

$\tilde{V}_\infty$ is the velocity without impurity. The smaller supersaturation (σ), the more pronounced the growth inhibition (pinning effect).

[4] $\tilde{\beta}$ is normalized step energy.



Cleaning by moving step



Terrace is periodically updated by steps. Impurities are removed from there or embedded into crystal. The fresh surface is impurity-free. If the sweeping period is shorter than the timescale of impurity adsorption, the surface is kept clean (impurity sweeping).

The faster the growth, the fewer the adsorbed impurities.

$$\bar{\theta} = 1 - \tilde{V}(1 - e^{-1/\tilde{V}}) \qquad (2)$$

Interdependency

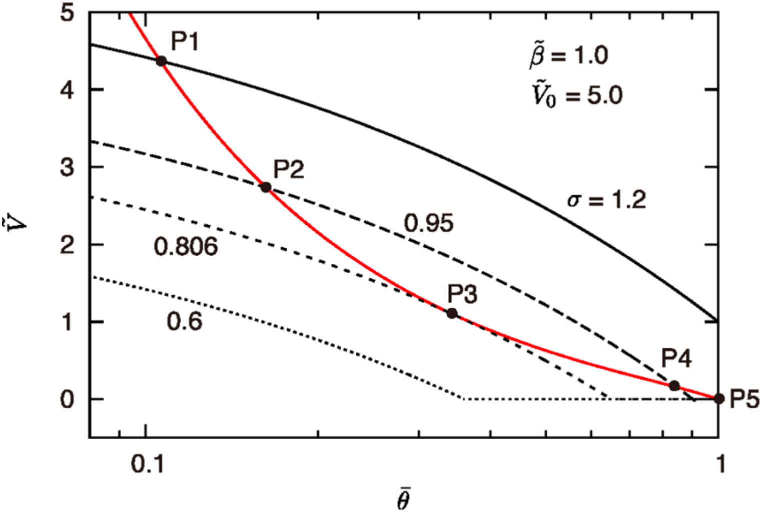
Positive feedback circuit

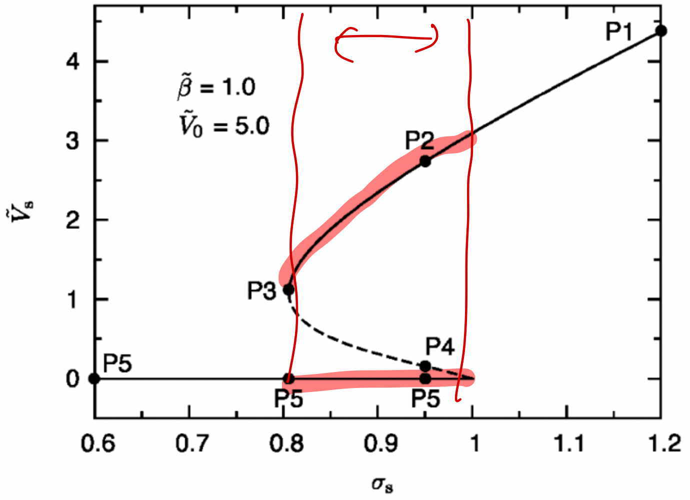
Increase (decrease) of ad-impurity ⇄ Decrease (increase) in step velocity

Growth rate decreases as impurities increase. The frequency of step passage decreases and the frequency of crystal surface update also decreases, which further increases the impurities (catastrophic pollution).

As the growth rate increases, the terrace renewal frequency increases and adsorbed impurities decrease. Thus, growth is further accelerated (growth spurt).

Steady solution

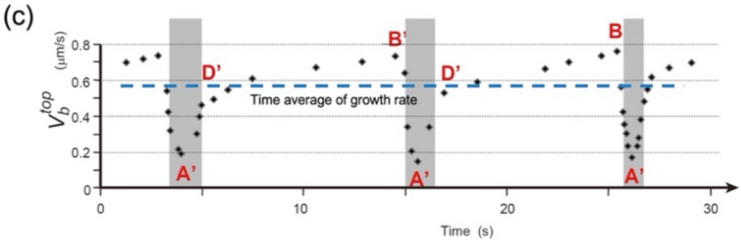




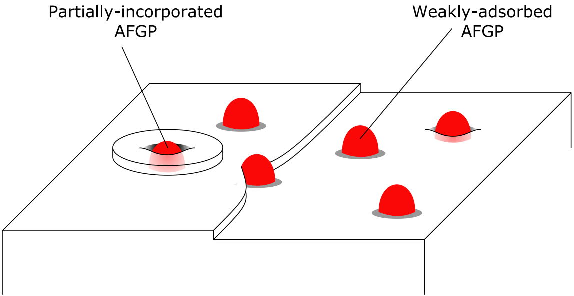
$\tilde{\beta}$ = 1.0
$\tilde{V}_0$ = 5.0
P1
P2
P3
P4
P5
P5
P5
0
1
2
3
4
$\tilde{V}_s$
0.6
0.7
0.8
0.9
1
1.1
1.2
σ_s

Question

The growth rate during rapid growth is a few times faster than that without AFGP8. This result cannot be explained by the growth hysteresis theory that only considers growth inhibition by impurities.



How can growth acceleration be taken into account?



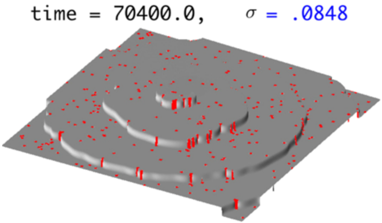
Hypothesis

Ad-AFGP inhibits step motion. However, when the portion is incorporated by steps, it induces nucleation.

Phase-field (PF) model for step dynamics

Height of surface is replaced by order parameter $\phi(\boldsymbol{r})$ (phase field). The step dynamics is simulated by solving the time variation of $\phi(\boldsymbol{r})$.[5]

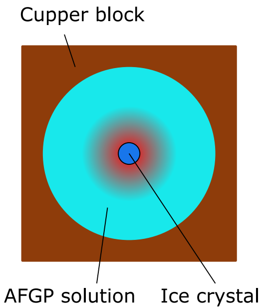
Random adsorption/desorption of impurities is calculated by Monte Carlo method.



PF simulation of spiral growth with impurities (red dots)

[5] Miura & Kobayashi (2015), *Cryst. Growth Des.* **15**, 2165; Miura (2015), *Cryst. Growth Des.* **15**, 4142; Miura (2016), *Cryst. Growth Des.* **16**, 2033; Miura (2020), *Cryst. Growth Des.* **20**, 245

Release of latent heat and its conduction



Ice crystal and growth cell

Time evolution of temperature distribution in AFGP solution[6]:

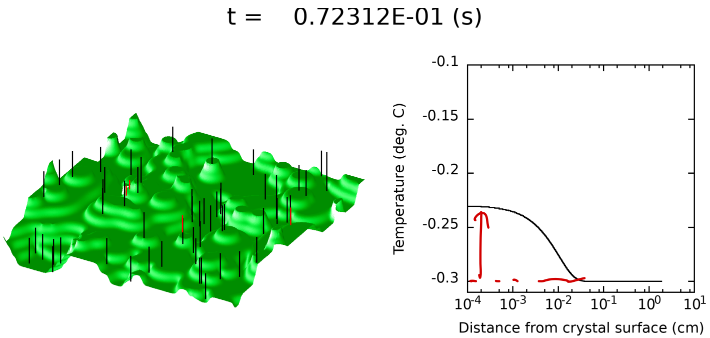
$$\frac{\partial T}{\partial t} = D_T \boldsymbol{\nabla}^2 T \qquad (3)$$

Solve by finite volume method.

- spherical symmetry
- release of latent heat as inner boundary condition
- constant supercooling at outer boundary

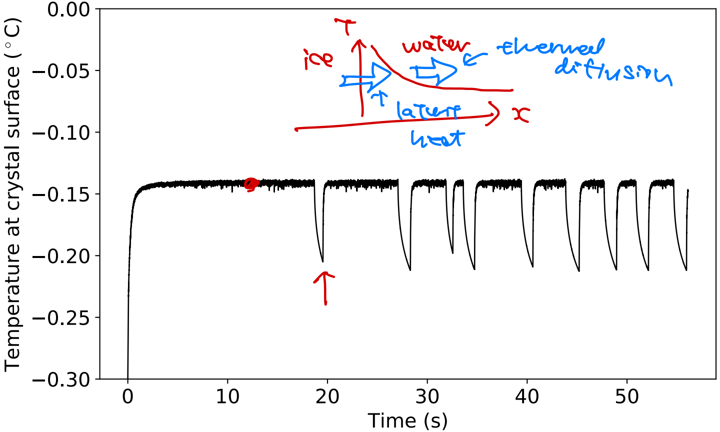
[6] D_T: thermal diffusivity

Calculation results



(Left) Crystal surface condition based on PF calculations. The lines represent AFGPs exposed on the crystal surface, black represents reversibly adsorbed AFGPs, and red represents irreversibly adsorbed AFGPs. (Right) Calculation results of the thermal diffusion equation. The horizontal axis represents the distance from the crystal plane on a logarithmic scale.

Time variation of interfacial supercooling



Reproduces oscillations with a period of $\sim$ 10 s!!

Discussion

- Impurities smaller than the critical radius do not induce heterogeneous 2D nucleation[7].
- In the experimental condition, the critical radius is estimated as $\sim$ 50 nm, which is larger than AFGP8 (a few nm)[8].

Issues

How does an AFGP smaller than the critical radius significantly promote basal surface growth? (aggregation of AFGP?[9])

[7] Zhang & Liu (2018), *Chem. Soc. Rev.* **47**, 7116
[8] Ahmed et al. (1975), *J. Biol. Chem.* **250**, 3344
[9] Qiu et al. (2019), *J. Am. Chem. Soc.* **141**, 7439

Summary and future

- The growth-promoting and -suppressing effects of AFGP adsorbed on ice-crystal surfaces were modeled and the step dynamics were numerically calculated by the phase-field method, combined with release of latent heat and its conduction.
- The model of heterogeneous nucleation in which AFGPs smaller than the critical radius become the “substrate” of a two-dimensional nucleus is inconsistent with previous findings. Reexamination is required.

Acknowledgement

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