Supplementary Information for

Step bunching instability of growing interfaces between ice and supercooled water

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Laser confocal microscopy combined with the vortex retarder. Even utilizing the temperature gradient system, the growth front moves fast, which requires an adjustment of a focus position during observations. Thus, it is highly difficult to make an adjustment of the differential interference contrast (DIC) of LCM-DIM after emergence of bunched steps together with an adjustment of the focus position. To evade this difficulty, we employ a new optical microscope based on the laser confocal system, which requires no contrast adjustment. As shown below, its resolution in the height direction reaches the order of an angstrom, whose resolution is comparable with that of LCM-DIM (1, 2). Hereafter, we remark on the detailed mechanism of this microscopy and compare the height resolution with LCM-DIM and AFM, using a gypsum (010) surface as a standard sample (see Materials and Methods in the main text).

In this microscopy, we employed a vortex retarder instead of the Nomarski prism. We simply replace the Nomarski prism by the vortex retarder. The insertion positions are same for each other (the so-called back focal plane of the objective). This optical device yields the optical vortex from the original Gaussian beam with linear polarization. The optical vortex beam made by this retarder has a donut-shaped intensity and azimuth polarization (see Fig. S1A).

Here we note that, when the step is present inside the vortex beam, interference occurs between the beam reflected from the upper and lower step side (Figs. S1B – D). This mechanism is reminiscent of that of DIM, utilizing two beams (ordinal and extra-ordinal light) decomposed by the Nomarski prism for interference. On the other hand, the step contrast obtained is different from each other. The LCM with vortex retarder shows basically a black contrast regardless of the height direction (upward or downward) of the step. This is because the original beam has no phase difference and the reference point for interference is set in the coherent condition (the zero-order interference position). In contrast, DIM shows white and black contrasts, depending on the height direction on the step because of the offset of the phase difference between the two beams, that is, the reference point for the interference, is adjustable with the Nomarski prism and is usually set at $\lambda/4$ (3). Although the contrast in the former is irrelevant with respect to the direction in the step height, no adjustment of the contrast is required, contrary to the latter, which makes our system more suitable for the observation of this system.

In Figs. S2A, B and C, we show a monomolecular step (shown by the arrow) on the gypsum (010) surface observed by LCM with the vortex retarder, and by conventional LCM-DIM and AFM, respectively. The inset in Fig. S2C shows a height profile of the arrowed step, measured by AFM. Its height is estimated as 7.6 Å, which proves that the step visualized indeed corresponds to a mono-molecular step. So, the height resolution of the new optical microscopy reaches the order of an angstrom just as well as does LCM-DIM and AFM. Finally, one may notice that the contrast of the step in Fig. S2A exhibits not black but DI-like contrast, contrary to the above explanation. Emergence of this contrast is natural, considering the situation that the surface and interface observed are tilted. In the above, we assume that the optical axis is completely normal to the surface and interface. However, if the surface and interface are tilted, even slightly, the phase difference between both step sides of the donut beam occurs after the reflection of light, in addition to that of the step.

Elastic step-step interaction. The elastic interaction between steps comes from elastic distortion induced by the step edge whose neighbour atoms are absent. This can be also interpreted as the interactions between force dipoles, aligning along each step. Here we calculate the elastic step-step interaction of this system, using the elastic properties of ice. For isotropic surfaces, the elastic interaction is known to be described as (4)

$$A_{el} = \frac{\pi^2}{6a^3} \frac{2(1-\nu^2)}{\pi E} (f^2 + t^2),$$  \hspace{1cm} [1]

where $\nu$ is the Poisson ratio, $E$ is the Young’s modulus, $f$ is the surface force dipole and $t$ is the surface stress tensor, respectively. Note that the basal face, the observation plane of this study, is isotropic. So, the employment of this equation is reasonable. Because the values of $f$ and $t$ are unknown, we put $f^2 + t^2 = (\gamma a)^2$, which comes from the assumption that the surface stress tensor is comparable to the surface tension. Substituting $\nu = 0.31$ and $E = 9.94 \times 10^9$ Pa (5) yields $A_{el}/a^3 = 2.8 \times 10^{-4}$ J/m$^2$ as the elastic contribution.

Entropic step-step interaction. The entropic interaction between steps comes from the reduction of entropy caused by the suppression of fluctuations of steps when steps approach each other. The entropic repulsion at equilibrium is known to be described as follows (6).

$$A_{en} = \frac{\pi^2}{6a^3} \frac{(k_B T)^2}{\beta_s},$$  \hspace{1cm} [2]

where $k_B$ is the Boltzmann constant and $\beta_s$ is the step stiffness. As described in the main text, strictly speaking, the entropic repulsion is coupled to the elastic interaction (see the above) (7). Considering the elastic contribution, one needs to add the linear correction term $\lambda^2 g$ in Eq. (2), which is defined as $(1 + \sqrt{1 - 2g})/2$, where $g = (2\tilde{\beta}_s A_{el})/(k_B T)^2$ (7). Employing $\beta_s = 3.4 \times 10^{-12}$ J/m (8) and $A_{el}$ obtained above, we obtained $g = 6.8 \times 10^{-3}$ for ice, i.e., $\lambda^2 g \sim 1$ ($T = 0$ °C), which means that influence of the elastic interaction is negligible in this system. Note that $g$ for Helium (0001) and Silicon (111) are estimated as $5.6 \times 10^{-11}$ and $4.0 \times 10^{-11}$, respectively. Finally, we obtained $A_{en}/a^3 = 1.4 \times 10^{-1}$ J/m$^2$ as the entropic contribution ($T = 0$ °C).

We further discuss non-equilibrium effects on the step fluctuations and its link to the entropic repulsion. Considering the entropic repulsion during the growth (non-equilibrium), one needs to take competition of timescales between step
advancement and step fluctuations into account. In our system, the characteristic time of the step advancing dynamics is defined as $t_c(k) \sim w_k/v_{st}$, where $w_k = \sqrt{(k_B T)/d_3 k^2}$ is a square of the step fluctuation width ($k$ being the wavenumber of a fluctuation along the direction parallel to the step and $d$ being the system size, $\sim 10^{-4}$ m). On the other hand, the relaxation time of the step fluctuation width is known to be described as $\tau(k) = A_0/(\Delta k^n)$, where $A_0$ and $n$ are a constant and an exponent depending on the mass transport mechanism of an isolated step (9). For melt growth, $n = 2$ is expected because the mass transport is dominated by a local attachment-detachment process. Thus, fluctuation modes below $k_c$, satisfying $\tau(k) > t_c(k)$, are frozen for advancing elementary steps, which diminishes the entropic repulsion through the suppression of the fluctuations. This may cause the large mismatch between the theoretical and experimental estimations of the entropic step-step interaction in this system.

**Electrostatic step-step interaction.** Here we derive the step-step interaction induced by permanent dipoles on the edge of steps. Because the interaction between individual permanent dipoles is proportional to $r^{-3}$ (see below), the resulting interaction between steps also becomes long-range, proportional to $r^{-2}$, whose exponent is same as that of the elastic and the entropic interaction. In the following, we give the expected value of a dipolar interaction and assess the exponent of its step-step interaction at the high temperature limit, rigorously considering the dipole structure of hexagonal ice lattice.

First, the electrostatic interaction between two individual dipoles (here, $i$, $j$, respectively) is described as

$$u_{ij}(r) = \frac{p^2}{4\pi\epsilon_0\epsilon_r} \frac{3(\hat{p}_i \cdot \hat{r})(\hat{p}_j \cdot \hat{r}) - (\hat{p}_i \cdot \hat{p}_j)}{r^3},$$

where $\epsilon_0$ is the dielectric constant of vacuum ($8.85 \times 10^{-12}$ F/m), $\epsilon_r$ is the relative dielectric constant of media ($\epsilon_r = 88$ for water at 0 °C (10)), $p$ is an absolute value of each dipole moment ($p = 1.855$ D for the water molecule (11)) and $\hat{r}$ is a vector between the points of two dipoles. Before defining the unit vector of dipole moments, we do that of four hydrogen bonds with the origin at the oxygen atom (Figs. S3A, B and Table S1). Note that $\epsilon_r$ is set along the $z$ direction, corresponding to the normal direction of the basal face. Because of proton disorder in hexagonal ice, hydrogen atoms can have four possible positions in the tetrahedral unit as long as they satisfy the so-called ice rule (12). So, the dipole moment in the tetrahedral unit can have six possible unit vectors as summarized in Fig. S3C and Table S2. In addition, we here set $\hat{r} = \hat{y}$ assuming that the distance between adjacent steps is 1. Note that $\hat{y}$ is a unit vector of the $y$ direction, $\hat{y} = (0, 1, 0)$. This makes Eq. (3) a simpler form as

$$u_{ij}(l) = -\epsilon_d(l)(3(\hat{p}_i \cdot \hat{y})(\hat{p}_j \cdot \hat{y}) - (\hat{p}_i \cdot \hat{p}_j)).$$

where $\epsilon_d = p^2/4\pi\epsilon_r^3$. Note that $\epsilon = \epsilon_0\epsilon_r$ is the dielectric constant of medium ($7.8 \times 10^{-10}$ F/m for water at 0 °C). Using Table S2, we can calculate the inner product in parentheses in Eq. (4) as summarized in Table S3. Table S3 tells us that there are four energy state in $u_{ij}(l)$, namely $-\epsilon_d(l)$, $-\epsilon_d(l)/2$, $\epsilon_d(l)/2$ and $\epsilon_d(l)$, respectively. So, we newly define these four states and their number as $u_k(l)$ and $D_k$ ($k = 1, 2, 3$ and $4$), respectively. Note that $D_k = 10, 8, 8$ and $10$ ($k = 1, 2, 3$ and $4$) as seen in Table S3. Using these definitions, the expected value of the dipolar interaction is straightforwardly given as follows.

$$\langle u(l) \rangle = \sum_{k=1}^{4} D_k u_k \exp\left(-\frac{u_k}{k_B T}\right) \sum_{k=1}^{4} D_k \exp\left(-\frac{u_k}{k_B T}\right).$$

Assuming $u_k \ll k_B T$, this equation is approximately described as

$$\langle u(l) \rangle \approx \sum_{k=1}^{4} D_k u_k \left(1 - \frac{u_k}{k_B T}\right) \sum_{k=1}^{4} D_k \left(1 - \frac{u_k}{k_B T}\right).$$

Employing $\sum_{k=1}^{4} D_k = D = D(=36)$, we obtain

$$\langle u(l) \rangle \approx \frac{\sum_k D_k u_k - \sum_k D_k u_k^2}{D \left(1 - \sum_k D_k u_k^2 / D k_B T\right)} \approx \frac{1}{D} \left[ \sum_k D_k u_k + \frac{1}{D k_B T} \left( \sum_k D_k u_k \right)^2 - \sum_k D_k u_k^2 \right] = \frac{2}{3k_B T} \epsilon_d(l)^2.$$  

Note that $\sum_k D_k u_k = 0$. Overall, we obtain the expected energy as $\langle u(l) \rangle = -(p^2/24\pi k_B T)$. Therefore, for the basal face of ice crystals, the dipolar interaction between steps becomes short-range attractive ($\propto l^{-6}$). In contrast, the long-range component is cancelled due to the high symmetry of the directions of the dipole moments in the hexagonal lattice. Although the rigorous calculation of the step-step interaction requires the integral including the angular dependence, we can say, at least,
that the resulting step-step interaction should be proportional to \( l^{-5} \), which is minor in comparison with the elastic and the entropic interactions, and thus is negligible.

In the above consideration, we assume that the probability of the six possible directions of the dipole moments is equivalent. However, taking the local interaction stemming from neighbouring dipoles into account, the dipoles may tend to align in a specific direction on average. Here, as a limiting case, we assess the step-step interaction, \( \phi(l) \), for a specific case that each dipole moment at the edge of the two neighbouring steps aligns in the same direction, perpendicular to their own step. Note that this condition yields the maximum value of the interaction. Although such a situation is rather unrealistic, it is useful to assess the order of its upper limit. In addition, we note that this assumption enables to easily integrate the dipolar interaction along the step, required when calculating the step-step interaction (see below).

There are two dipole moments (here \( \hat{p}_1z \) and \( \hat{p}_6 \)), corresponding to this situation, that is, having no vector component in the direction along with the step (the \( x \) direction). Here, we decompose them into the normal \( (p_{\perp}) \) and the plane \( (p_{\parallel}) \) components to the basal face \( (p = p_{\perp} + p_{\parallel}) \). Employing the decomposition, we can rewrite Eq. (3) as follows.

\[
u(x) = - \frac{p^2}{4\pi\epsilon} \left( \frac{3(\hat{p}_{\parallel} \cdot r)^2}{r^5} - \frac{1}{r^4} \right) .\]

[8]

Note that the normal component is cancelled because \( r \) and \( p_{\perp} \) are orthogonal and its inner product becomes zero. For the calculation of the step-step interaction, the interaction pair of a dipole is located at any point on a step edge. Thus, in Eq. (8), we specifically give \( |r| = (x^2 + l^2)^{1/2} \) and \( p_{\parallel} \cdot r = l/(x^2 + l^2)^{1/2} \), respectively. As a result, we can represent \( u(r) \) as a function of \( x \) as follows.

\[
u(x) = - \frac{p^2}{4\pi\epsilon} \left( \frac{3\hat{p}_{\parallel}^2 l^2}{(x^2 + l^2)^{3/2}} - \frac{1}{(x^2 + l^2)^{3/2}} \right) .\]

[9]

Note that \( \phi(l) \) is derived by the integral of \( u(x) \),

\[
\phi(l) = - \int_{-\infty}^{\infty} dx \frac{p^2}{4\pi\epsilon} \left( \frac{3\hat{p}_{\parallel}^2 l^2}{(x^2 + l^2)^{3/2}} - \frac{1}{(x^2 + l^2)^{3/2}} \right)
= - \frac{2\pi^2 p^2}{4\pi\epsilon l^2} (-2\hat{p}_{\parallel}^2 + 1), \]

[10]

where \( \sigma \) is the number of dipoles in the unit length (here, the inverse of the elementary height of the prism face, \( 2.6 \times 10^9 \) m\(^{-1}\)). Because of \( p_{\parallel} = (0, \sqrt{2/3}, 0) \) for \( \hat{p}_1 \) and \( (0, -\sqrt{2/3}, 0) \) for \( \hat{p}_6 \), we obtain \( p_{\parallel}^2 = 2/3 \) for both cases. Overall, \( \phi(l) \) is given by the following form,

\[
\phi(l) = - \frac{\sigma^2 p^2}{6\pi\epsilon} l^{-2}. \]

[11]

This means that \( A/a^3 \) for the electrostatic step-step interaction is given by \( -\sigma^2 p^2/6\pi\epsilon a^3 = -3.4 \times 10^{-4} \) J/m\(^2\). We stress that, even in the limiting case, the absolute value is the same order as that of the elastic interaction (\( 2.8 \times 10^{-4} \) J/m\(^2\)).

**Step spacing of bunched steps for the spiral growth.** Here we derive the step spacing of bunched steps for the spiral growth and then show that the expression of Eq. 3 in the main text does not depend on whether the step is elementary or bunched. As shown below, this comes from the simple fact that the radius of two-dimensional critical nuclei, \( R_e \), is the same for bunched and elementary steps. Here, note that the step spacing for the spiral growth obeys \( l_{st} = 19R_e \).

The volume of a two dimensional island of a bunched step, composed of \( n \)-elementary steps, is written as \( V = \pi R^2 n a \), where \( R \) is the radius of the island and \( a \) is the height of an elementary step. The number of the molecules in this island is described as \( N = V/\Omega = \pi R^2 n/\Omega \), where \( \Omega \) is the surface area occupied by one molecule. Thus, we obtain the free energy barrier of the two-dimensional nucleation of the bunched step as

\[
\Delta G = - \frac{\pi R^2 n}{\Omega} \Delta \mu + 2\pi R \beta_{ha}, \]

[12]

where \( \beta_{ha} \) is the step free energy of the bunched step. Note that \( R_e \) corresponds to \( R \) maximizing \( \Delta G \), which is given as \( R_e = \Omega \beta_{ha}/n \Delta \mu \). Assuming that \( \beta_{ha} \approx n \beta \) (\( \beta \) being the step free energy density of an elementary step), we see that the factor \( n \) is canceled and obtain \( R_e = \Omega \beta/\Delta \mu \), which is identical to \( R_e \) of the elementary step. Therefore, the step spacing of the spiral growth, obeying \( l_{st} = 19R_e \), is the same for bunched and elementary steps.
Fig. S1. Laser confocal microscopy with the vortex retarder. (A) A schematic of the transformation of the beam profile and the polarization state through the vortex retarder. In the vortex retarder, the arrows indicate the fast axis orientation. (B) A donut beam illuminating a step (a top view). (C) A side view. Here, the step height is $\Delta$. (D) A schematic view of the phase difference between both step side of the beam. Note that each line color (gray and blue) corresponds to that coloured in (C).
Fig. S2. Gypsum (010) surface observed by LCM with the vortex retarder, LCM-DIM and AFM. (A), (B) and (C) show the images of LCM with the vortex retarder, LCM-DIM and AFM, respectively. The inset of (C) indicates the height profile (the lateral direction) averaged along the blue line. Note that the value of 7.6 Å corresponds to the mono-molecular step height of the gypsum (010) surface. Thus, the step indicated by the blue arrows in (A) and (B) corresponds to the mono-molecular step.
Fig. S3. The definition of unit vectors of four hydrogen bonds with the origin at the oxygen atom. (A) Its schematic. (B) A top-plane view of the four-unit vectors. (C) A top-plane view of the unit vectors of six-possible hydrogen bonds.
Table S1. The definition of the unit vectors of the four hydrogen bonds with the origin at the oxygen atom.

|   | $(x, y, z)$                          |
|---|-------------------------------------|
| $e_a$ | $(\frac{2}{\sqrt{6}}, \frac{\sqrt{2}}{3}, -\frac{1}{3})$ |
| $e_b$ | $(-\frac{2}{\sqrt{6}}, -\frac{\sqrt{2}}{3}, -\frac{1}{3})$ |
| $e_c$ | $(0, -\frac{2\sqrt{2}}{3}, -\frac{1}{3})$ |
| $e_d$ | $(0, 0, 1)$ |
Table S2. The definition of the unit vectors of the six possible dipole moments, satisfying the ice rule.

| \( \hat{p}_i \) | \((x, y, z)\) |
|----------------|----------------|
| \( \hat{p}_1 \) | \(0, \sqrt{\frac{3}{2}}, -\frac{1}{\sqrt{3}}\) |
| \( \hat{p}_2 \) | \(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{3}}\) |
| \( \hat{p}_3 \) | \(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{3}}\) |
| \( \hat{p}_4 \) | \(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{3}}\) |
| \( \hat{p}_5 \) | \(-\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{3}}\) |
| \( \hat{p}_6 \) | \(0, -\sqrt{\frac{3}{2}}, \frac{1}{\sqrt{3}}\) |
Table S3. The inner products in parentheses in Eq. (4).

| i \ j | 1  | 2  | 3  | 4  | 5  | 6  |
|-------|----|----|----|----|----|----|
| 1     | 1  | -1 | -1 | 1  | 1  | -1 |
| 2     | -1 | -\frac{1}{2} | \frac{1}{2} | \frac{1}{2} | -\frac{1}{2} | 1  |
| 3     | -1 | -\frac{1}{2} | -\frac{1}{2} | -\frac{1}{2} | \frac{1}{2} | 1  |
| 4     | 1  | \frac{1}{2} | -\frac{1}{2} | -\frac{1}{2} | \frac{1}{2} | -1 |
| 5     | 1  | -\frac{1}{2} | \frac{1}{2} | -\frac{1}{2} | -\frac{1}{2} | -1 |
| 6     | -1 | 1  | 1  | -1 | -1 | 1  |
Movie S1. Spatiotemporal dynamics of the SBI (Movie of Fig. 3A).

Movie S2. Spatiotemporal dynamics of terminations and bifurcations of bunched steps (Movie of Fig. 3B).

Movie S3. A birth of the spiral growth mode induced by the SBI (Movie of Fig. 6).

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