

1 **Sea water frozen crystallisation impacted by flow and**  
2 **heterogeneous nucleation: PFM-LBM coupled**  
3 **modelling, simulation and experiments**

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18 **Abstract**

19 This study presents a novel phase field method (PFM) - lattice Boltzmann method (LBM)  
20 coupled model that describes the ice crystal growth in sea water freezing. Sea water frozen  
21 crystallisation impacted by flow and heterogeneous nucleation was numerically and experimentally  
22 investigated. The PFM-LBM model was established to conduct simulation. A microscope  
23 observation experimental system was built to conduct verification. The results show that flow of sea

24 water effectively promotes the diffusion of discharged salt and the growth of ice crystals, and  
25 reduces the probability of dendrite closure. In the directional competitive growth of ice crystals, the  
26 salt content trapped in the ice crystals decreased by 17.4% at 0.025 m/s and 21.9% at 0.05 m/s, while  
27 the existence of heterogeneous particles resulted in a narrower the brine channel and higher ice  
28 crystal growth rate, of which the ice crystal area increased by 10.8% and the trapped salt content in  
29 the ice crystals decreased by 14.8%. The study provides both a methodology of numerically simulate  
30 sea ice crystallisation which includes the phase change, solute migration, heat transfer and flow, and  
31 a feasible controlling approach to improve desalination efficiency of sea water frozen crystallisation.

32 **Keywords: Freeze desalination; Phase field method; LBM; Heterogeneous nucleation**

33

### Nomenclature

#### *Symbols*

$c$	Equilibrium concentration, $\text{kg kg}^{-1}$
$C_p$	Specific heat, $\text{J kg}^{-1} \text{K}^{-1}$
$D$	Diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$e$	Velocity component
$F$	Free energy, J
$f$	Surface free energy density, $\text{J m}^{-3} \text{mol}^{-1}$
$g$	Double-well potential
$h$	Monotonously changing function
$J$	Heat flux
$K_T$	Thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
$L$	Latent heat, $\text{kJ m}^3$
$M$	Phase-field mobility
$Q$	Heat per unit volume, $\text{w m}^{-3}$
$R$	Gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
$r$	Vector direction
$T$	Temperature, K

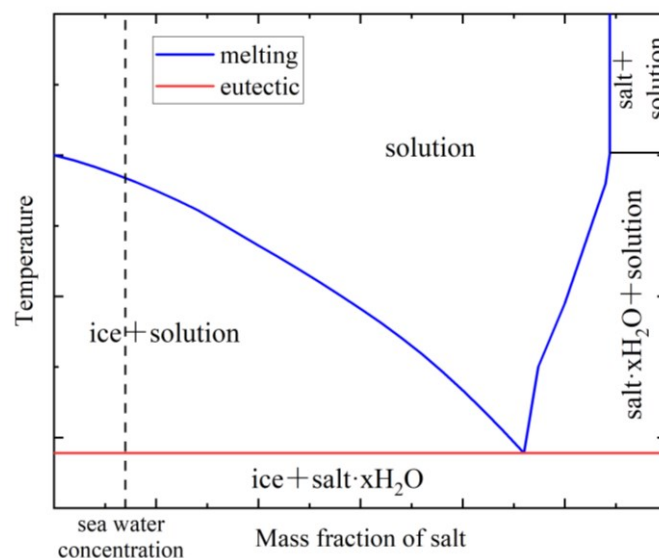
$u$	Velocity, m s <sup>-1</sup>
$V_m$	Molar volume, m <sup>3</sup> mol
$\bar{V}$	Velocity correction term
$W$	Height of the double-well potential
<i>Greek Symbols</i>	
$\alpha$	Direction
$\delta_x$	Space-step, m
$\delta_t$	Time-step, s
$\rho$	Density, kg m <sup>3</sup>
$\tau$	Dimensionless relaxation time, s
$\phi$	Phase-field variable
$\omega$	Weight function
<i>Superscripts/Subscripts</i>	
$cc$	Bulk solid and liquid
$eq$	Equilibrium
$S$	Solid
$ss$	Speed of sound, m s <sup>-1</sup>
$L$	Liquid
<i>Acronyms</i>	
PFM	Phase field method
LBM	Lattice Boltzmann method

34

## 35 **1 Introduction**

36 Sea water desalination is a key measure to solve the shortage of freshwater resources. Currently,  
 37 the most widely used sea water desalination methods are membrane-based methods and distillation-  
 38 based methods [1,2], which require a large amount of energy during freshwater production. Freezing  
 39 desalination [3] method, by contrast, consumes lower energy because it utilizes the temperature  
 40 difference between water and salt crystallisation to separate ice from sea water and the latent heat

41 of melting (334.7kJ/kg at 1 atm) only 1/7 of that of evaporation (2259.4kJ/kg at 1 atm) [4,5]. The  
42 freeze desalination methods generally fall into two categories: direct contact freezing and indirect  
43 contact freezing. Direct contact freezing may cause the refrigerant contamination of water products  
44 and concentrated brine during freeze desalination due to the probability of hydrate formation [6],  
45 while indirect contact freezing can avoid this pollution because the sea water and refrigerants are  
46 separated in the crystallizer. Common routes of indirect contact freezing method include suspension  
47 and layer freeze crystallisation [7]. It is noted that in suspension freeze crystallisation the sea ice  
48 and sea water are mixed together, where the adhering brine on ice slurry surface make it difficult to  
49 effectively separate the sea water from the sea ice [8]. Experiments conducted in reference [9] show  
50 that the minimum salinity of seawater can merely be reduced from 35ppt to approximately 20ppt  
51 with suspension freeze crystallisation method. In comparison, in layer freeze crystallisation larger  
52 volume of the ice crystals are formed during the gradual growth of the ice layer, which means the  
53 adhering brine on ice layer surface can be reduced and the desalination can be more effective.



54

55 **Fig. 1.** Salt solution phase diagram

56

57 Although freezing desalination have shown a promising prospect, it still faces great difficulties  
58 in sea ice purification. The problem lies in sea ice crystallisation mechanism. Fig. 1 shows the salt  
59 solution phase diagram. By controlling sea ice crystallisation temperature above the eutectic  
60 temperature of water and salt, pure water will crystallise first, so theoretically the water can be  
separated by freezing desalination method. However, the pockets of concentrated brine are trapped

61 within ice crystals (named brine pockets) which are hard to remove [10]. This phenomenon results  
62 in high concentration in sea ice [11,12], therefore post-treatment technique is needed to purify sea  
63 ice. Main purification methods include water washing and centrifugation. However, water washing  
64 methods require large amount of fresh water which usually takes up 50% of produced raw ice weight  
65 [13], while centrifugation methods need extra power-driven centrifugation and sweetening process [14]  
66 to effectively purify the sea ice. These purification techniques are not yet fully effective in terms of  
67 cost, large water-handling capacity, and ice net output, and the industrial scale application of  
68 freezing desalination remains difficult.

69 Another option is to conduct pre-treatment technique rather than post-treatment technique and  
70 the key point is to inhibit the formation of brine pockets by controlling crystallisation condition.  
71 Pre-treatment technique for sea water freeze desalination is in development. Current researches  
72 mainly focus on experimental approaches including layer-freezing [15], spray-freezing[16],  
73 vertical-freezing [17], radial-freezing [18], suspension crystallisation [19] and ice seeds induced  
74 nucleation [13]. These investigations indicate that homogeneous/heterogeneous nucleation mode,  
75 crystallisation temperature and heat flux direction all impact the freeze desalination efficiency.  
76 These experimental researches have made great contribution in pointing out the way of improving  
77 desalination efficiency, nevertheless, the microscopic mechanisms of brine pockets formation and  
78 inhibition during the growth of sea ice is still not totally understood. The reason is that the  
79 complicated physical processes in freeze desalination such as phase change, solute migration, heat  
80 transfer and flow [20] can hardly be thoroughly explained with the macroscopic experiments.

81 It is worth noting that the phase-field method (PFM) [21] based on the Ginzburg-Landau theory  
82 [22] and statistical physics [23] have been developed to solve crystallisation problem [24,25]. PFM  
83 employs a concept of diffuse interface instead of traditional sharp interface and utilizes an order  
84 parameter to describe the probability of atoms occupying lattice positions within interface. With  
85 these two efforts, it no longer needs to precisely describe the complicated two-phase sharp interface  
86 of crystals, and this make the crystallisation simulation possible. PFM has shown success in the  
87 prediction of metal solidification. But so far, few studies have applied this method to sea water ice  
88 crystallisation simulation. In 2013, Berti [26] attempted to rise a phase field model to describe the  
89 ice-liquid phase transition in brine channels in sea ice, and the feasibility of PFM in sea ice

90 simulation was strictly proved for the first time. In 2016, van der Sman [27] present the first model  
91 ever that describes the ice freezing phase change in a sugar solution. In 2019, Han [28] attempted  
92 to use a Wheeler model to simulate the morphology of ice in binary water-salt. In 2020, our previous  
93 work [29] successfully simulated the process of free crystallisation of single crystal nuclei,  
94 competitive crystallisation of multi-nuclei, and oriented nuclei in a NaCl-H<sub>2</sub>O binary solution based  
95 on KKS phase-field model [30]. In 2021, van der Sman [31] established a multiscale simulation  
96 model to simulate the directional ice crystal morphology in sugar solutions. However, above  
97 proposed models are not entirely satisfactory, because the flow governing equations are not  
98 considered in numerical model, making them unable to reveal the impact of fluid convection on sea  
99 ice crystallisation. Besides, in these studies sea ice crystal is assumed to experience a homogeneous  
100 nucleation process, and the influence of heterogeneous nucleation on sea ice crystal is still not clear.

101 In this study, we present a novel phase field method (PFM) - lattice Boltzmann method (LBM)  
102 coupled model to conduct numerical simulation of sea ice crystallisation. The purpose of this study  
103 is to provide a methodology of numerically simulate sea ice crystallisation which includes the phase  
104 change, solute migration, heat transfer and flow, as well as a feasible controlling approach to  
105 improve desalination efficiency of sea water frozen crystallisation. Both the single sea ice  
106 crystallisation which reflects the suspension freeze crystallisation and the directional competitive  
107 sea ice crystallisation which reflects the layer freeze crystallisation were investigated. The  
108 crystallisation of sea water at different flow rates and the influence of heterogeneous particles on  
109 sea ice crystal morphology, solute diffusion, and desalination efficiency were compared, and key  
110 parameters such as the tip growth rate and ice crystal area were analysed. A high-definition three-  
111 dimensional transmission microscope observation experimental system was built to conduct  
112 experimental verification. The impact of sea water flow and heterogeneous nucleation on single/  
113 directional sea ice crystallisation and freeze desalination efficiency were analysed.

## 114 **2 Mathematical model**

### 115 **2.1 Phase field model coupling with velocity corrective term**

116 The phase-field model is used to couple the phase, solute and temperature fields in the  
117 crystallisation process to visualise the crystallisation process and demonstrate the formation process  
118 of dendrites directly [32]. The free energy function or entropy function [33] can be combined with

119 the Ginzburg-Landau theory to derive the phase-field governing equation. Because the expression  
120 is not unique, there are multiple phase-field models. This study adopted the KKS phase-field model  
121 based on the free energy density function. The KKS phase-field model was revised to construct an  
122 ice crystallisation phase-field model suitable for sea ice crystallisation.

### 123 2.1.1 Phase field governing equation

124 Based on the Ginzburg-Landau free energy theory [34], for a closed system with a volume of  
125  $V$ , the free energy  $F$  can be expressed as:

$$126 \quad F = \int_V \left[ f(\phi, c, e) + \frac{1}{2} \varepsilon^2 (\nabla \phi)^2 + \frac{1}{2} \delta^2 (\nabla c)^2 \right] dV \quad (1)$$

127 where  $f(\phi, c, e)$  is the chemical free energy density[35],  $\phi$  is the phase-field variable defined as a  
128 continuous variable between the solid ( $\phi = 1$ ) and liquid ( $\phi = 0$ ) phases, as well as  $0 < \phi < 1$  at the  
129 solid-liquid interfacial phase;  $c$  is the concentration field variable, and  $\varepsilon$  and  $\delta$  are the gradient  
130 energy coefficient related to the interface anisotropy [35].

$$131 \quad f(c, \phi, e) = h(\phi) f^S(c_S) + (1 - h(\phi)) f^L(c_L) + Wg(\phi) \quad (2)$$

$$132 \quad h(\phi) = \phi^3 (10 - 15\phi + 6\phi^2) \quad (3)$$

$$133 \quad g(\phi) = \phi^2 (1 - \phi)^2$$

$$134 \quad (4)$$

135 Here,  $h(\phi)$  is the monotonously changing function [36] from  $h(\phi) = 0$  to  $h(\phi) = 1$ ,  $g(\phi)$  is the double-  
136 well potential;  $W$  is the height of the double-well potential;  $f^S$  and  $f^L$  are the chemical potentials of  
137 the solid and liquid, respectively; and  $c_S$  and  $c_L$  are the equilibrium concentrations of the solid and  
138 liquid, respectively.

139 According to the principle of entropy increase, the free energy gradually tends to decrease until  
140 it reaches equilibrium [37]. According to the minimum free energy theory, the Lyapounov function  
141 [38] with variational form and the dynamic theory with linear irreversibility can be derived as  
142 follows.

143 The phase-field governing equation of the KKS model [30] is:

$$144 \quad \frac{\partial \phi}{\partial t} = M[\nabla(\varepsilon^2 \nabla \phi) - f_\phi] \quad (5)$$

145 where  $M$  is the phase-field mobility;  $f_\phi$  is the partial derivative of the free energy density with respect  
146 to the phase-field parameter.

147 Because the phase field is not directly affected by the velocity field, the governing equation of  
148 the phase field [30,39] is defined as:

$$149 \quad \frac{\partial \phi}{\partial t} = M[\varepsilon^2 \nabla^2 \phi - \frac{\partial}{\partial y}(\varepsilon(\theta) \varepsilon'(\theta) \frac{\partial \phi}{\partial x}) + \frac{RT}{V_m} h'(\phi) \ln \frac{(1-c_L^e)(1-c_S)}{(1-c_S^e)(1-c_L)} - Wg'(\phi)] \quad (6)$$

150 where  $c_S$  and  $c_L$  are the equilibrium compositions of solid and liquid, respectively.

151 The concentration-field equation coupled with the phase field equation[30] is described in the  
152 form of the free energy density:

$$153 \quad \frac{\partial c}{\partial t} = \nabla \left( \frac{D(\phi)}{f_{cc}} \nabla f_c \right) \quad (7)$$

154 where  $D(\phi)$  is the diffusion coefficient dependent on the phase field, and  $f_{cc}$  was added to guarantee  
155 a constant diffusion coefficient for both the bulk solid and liquid.

156 Approximate treatment [40] with dilute solution:

$$157 \quad D(\phi) = h(\phi) D_S + [1 - h(\phi)] D_L \quad (8)$$

$$158 \quad \nabla f_c = \nabla \frac{RT}{V_m} \ln \frac{c_L}{(1-c_L)} \quad (9)$$

$$159 \quad f_{cc} = \frac{f_{c_L c_L} f_{c_S c_S}}{[1 - h(\phi)] f_{c_S c_S} + h(\phi) f_{c_L c_L}} \quad (10)$$

$$160 \quad f_{c_L c_L} = \frac{RT}{V_m} \frac{1}{c_L (1-c_L)} \quad (11)$$

$$161 \quad f_{c_S c_S} = \frac{RT}{V_m} \frac{1}{c_S (1-c_L)} \quad (12)$$

162 The countercurrent behaviour of sea water affects the distribution of salt concentration in sea  
163 water, and the influence of flow should be expressed in the governing equation of the concentration  
164 field [41]. Assuming that the position of the ice crystals is fixed, the ice crystals generated will not  
165 be deformed by the flow pressure difference. The velocity correction term is added to the  
166 concentration field control equation to obtain the concentration field control equation coupled with



167 the velocity field:

$$168 \quad \frac{\partial c}{\partial t} + \nabla \cdot (\bar{V}c) = \nabla [D(\phi) \nabla c] + \nabla [D(\phi) h'(\phi)(c_L - c_S) \nabla \phi] \quad (13)$$

### 169 **2.1.2 Temperature field governing equation**

170 It is assumed that the density, specific heat, and thermal conductivity of the solution are  
171 constant during the crystallisation process [42]. Considering the release of latent heat of  
172 crystallisation, according to the standard heat conduction equation, the following formula is  
173 obtained:

$$174 \quad \frac{\partial Q}{\partial t} + \nabla \cdot J_Q = 0 \quad (14)$$

$$175 \quad J_Q = -K_T \nabla T \quad (15)$$

176 where  $Q$  is the heat per unit volume,  $J_Q$  is the heat flux, and  $K_T$  is the thermal conductivity.

177 Considering the change in entropy of the solid–liquid interface, the change in heat per unit  
178 volume per unit time [42] can be expressed as:

$$179 \quad \frac{\partial Q}{\partial t} = C_p \frac{\partial T}{\partial t} - \frac{L}{2} \frac{\partial h(\phi)}{\partial t} \quad (16)$$

180 where  $C_p$  is the specific heat and  $L$  is the latent heat.

181 As the flow of sea water increases the original natural convection of the sea water, the  
182 disturbance in the sea water increases, which affects the latent heat released by the ice crystals. Thus,  
183 the increase in sea water disturbance promotes the latent heat transfer process. The temperature field  
184 control equation of the velocity field coupled with the velocity correction term [30] is expressed as:

$$185 \quad \frac{\partial T}{\partial t} + \nabla \cdot (\bar{V}T) = D_T \nabla^2 T + \frac{1}{2} \frac{L}{C_p} \frac{\partial h(\phi)}{\partial t} \quad (17)$$

### 186 **2.3 Flow model**

187 The lattice Boltzmann method (LBM) [43] was used to solve the convection during sea ice  
188 crystallisation. The two-dimensional, nine-speed model (D2Q9) [44] was selected to conduct  
189 simulation. In addition, the fluid flow is considered as incompressible single-phase flow and the  
190 flow field is described by a typical single-phase LBM model, which can be found in our previous  
191 study [43,44] and other similar study [45,46].

## 192 3 Numerical and experimental methods

### 193 3.1 Physical model and boundary condition

194 Ice crystal growth in sea water under both natural convection and force convection conditions,  
195 with a domain of  $1600 \times 1600$  meshes simulated, were simulated in this research. Unit mesh size is  
196  $0.07\mu\text{m}$ . To avoid the accumulated latent heat affecting the calculation domain [47], the Neumann  
197 temperature boundary conditions instead of zero Neumann boundary conditions are selected. For  
198 single sea ice crystals, the location of the circular initial crystal nucleus was set at the centre of the  
199 simulation area, with the diameter of  $10dx$ . The initial temperature of the simulated area was 285.15  
200 K. In addition, the temperature of sea water flowing into the simulation area was set at 285.15 K.  
201 Additionally, when temperature changes from 273K to 285K, the thermal conductivity changed by  
202 2.9%, density changed by 0.072% (seen on Appendix. A), which has no obvious effect on the  
203 thermophysical properties. The detailed physical parameters and initial condition are shown in Table  
204 1.

205  
206 **Table. 1.** Physical parameters and initial condition in simulation

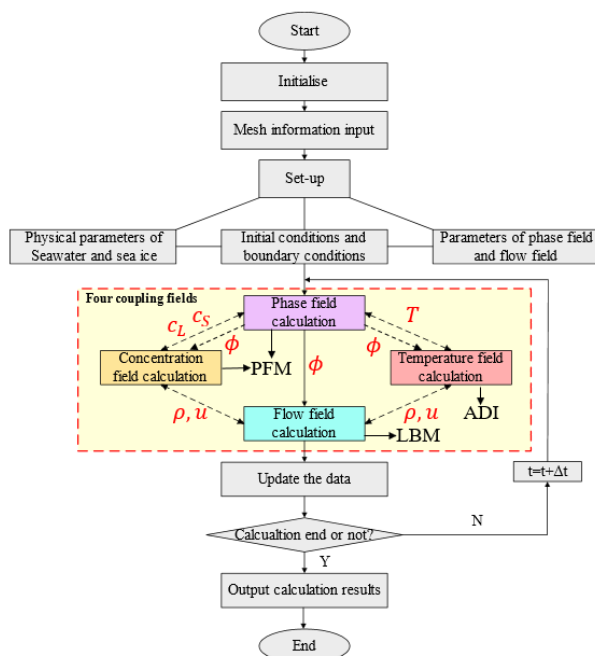
Physical parameters	Water-NaCl binary solutions
Interface Energy $\sigma$ , J/m <sup>2</sup>	0.0758
Latent Heat $L$ , kJ/kg	335
Equilibrium Constant $k^e = c_L^e / c_S^e$	0.075
Salinity Mass Concentration $C$ , g/kg	0.03
Mesh Number in x axis direction	1600
Mesh Number in y axis direction	1600
Unit Mesh Size, $\mu\text{m}$	0.07
Time Step, $\mu\text{s}$	1.72
Mesh Size of Initial Crystal Nucleus Radius	10
Initial Subcooling Degree of Temperature $\Delta T$ , K	15
Heat flux $\sigma$ , J/(m <sup>2</sup> ·s)	$2 \times 10^5$

207

### 208 3.2 Numerical simulation methods

209 The C++ programming language was used to compile the established model, and the main  
210 calculation was divided into the following parts:

- 211 1 Establishing a sea water physical parameter database.  
 212 2 Constructing a basic solution grid matrix.  
 213 3 Setting initial conditions, boundary conditions, and phase-field and flow-field parameters.  
 214 4 Calculating governing equations for the phase, solute, and temperature fields.  
 215 5 Substituting the calculation results into the LBM solving module, and returning to the flow-  
 216 field distribution after the calculation is complete.  
 217 6 Calculating the ice crystal growth parameters.  
 218 7 Saving calculation results.  
 219 The numerical solution strategy is shown in Fig. 2.



220

Fig. 2. Numerical solution strategy

221

222 The PFM is used to calculate phase field and temperature field, and LBM is applied in solving  
 223 the flow field. Additionally, the coupled method of PFM and LBM is as following:

224 Step 1, carry out initialization and boundary setting.

225 Step 2, calculate phase field and concentration field by PFM, and calculate temperature field  
 226 by finite difference method (ADI).

227 Step 3, Exchange information ( $C_L, C_S, T, \rho, u, \phi$ ) of each field.

228 Step 4, calculate flow field using LBM until the flow domain reaches quasi equilibrium state

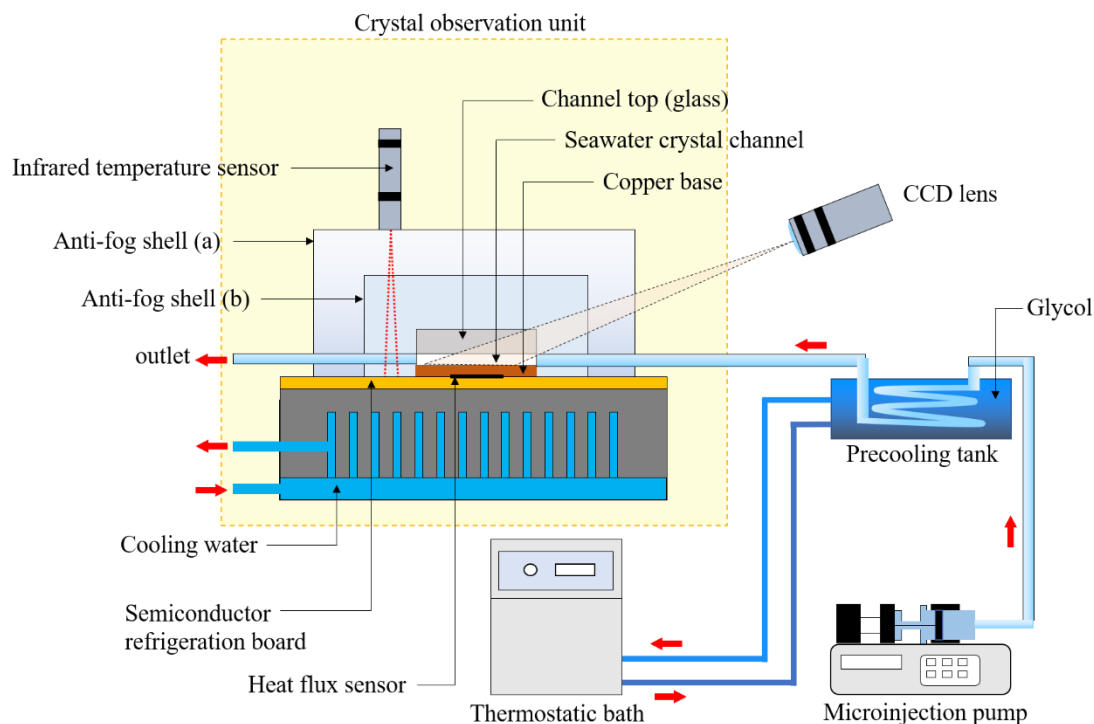
$$229 \quad \left( \frac{\sqrt{\sum_x \sum_y [u(x,y,t) - u(x,y,t-1)]^2}}{\sqrt{\sum_x \sum_y [u(x,y,t)]^2}} < 10^{-5} \right).$$

230 Step 5, loop step 2-4 until the simulation reaches the target condition.

231 The solid domain is represented in the model as follows: in phase field,  $\phi$  is set as 1; in  
232 concentration field, the concentration is set as 0; in flow field, the density and velocity are set as 1  
233 (can be adjusted according to real physical parameter) and 0, respectively. The solid-fluid  
234 boundaries in phase field, concentration field and temperature field are solved by PFM, while it is  
235 solved by bounce-back boundary of LBM in flow field. In addition, the growing ice crystal is also  
236 considered as solid, which is also solved by this method. In this study, the solid particle and ice  
237 crystal are all considered as solid domain. In phase field calculation, the order parameter of the two  
238 solid domain is set to 1 and the particles are pre-placed in the simulation area during initialization,  
239 and its boundary will not change during simulation. Because the order parameter to describe the  
240 probability of atoms occupying lattice positions within interface, the interface between ice and  
241 solution is can be described by the calculated order parameter, then the solid region of ice crystals  
242 is always changing due to the growth of ice crystals.

### 243 **3.3 Experimental setup and plan**

244 A high-definition three-dimensional transmission microscope observation experimental system  
245 was used to verify the simulation results. The schematic diagram is shown in Fig. 3.



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**Fig. 3.** Schematic diagram of experimental system

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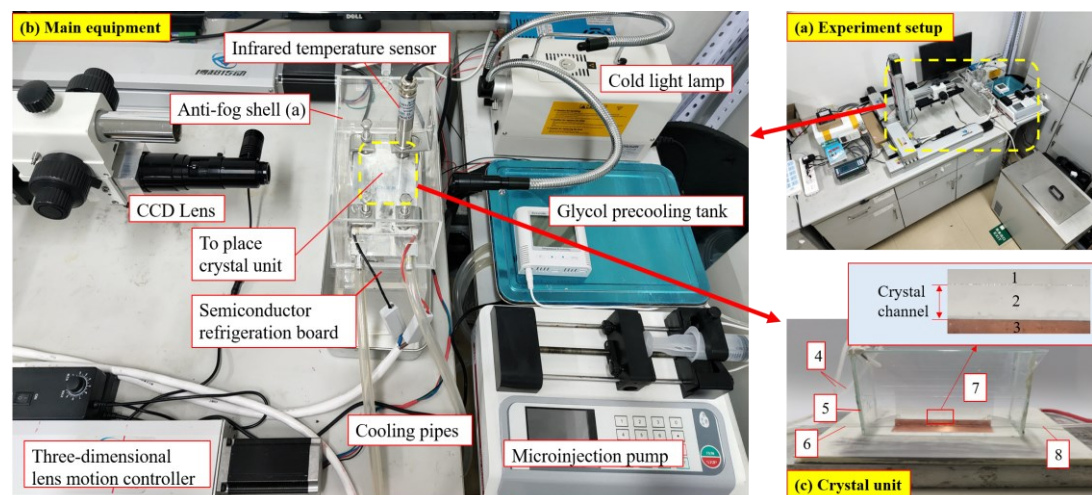
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259

260

The experimental system mainly consists of the crystal observation unit, the transmission microscope and the auxiliary devices. The sea ice crystal channel, in which the sea water get freeze, is sandwiched between top glass and bottom copper base. The copper base is placed on the semiconductor refrigeration board, so that inverse heat flux is applied to the sea ice crystal channel. The heat flux sensor is placed between copper base and semiconductor to measure heat flux during sea ice crystallisation. Besides, the crystal observation unit is covered by two shells, in which the helium is filled to create an anti-fog and adiabatic environment. Both the glass top and copper bottom of the channel wall have been mechanically smoothed to avoid the influence/contamination (i.e. e.g. surface roughness) on the freezing process. In addition, a microinjection pump and a precooling tank are used to preciously control the flowrate and temperature of sea water into the crystal unit, respectively. A high-definition transmission microscope moved by the three-dimensional lens motion controller is used to observe the crystallisation process of sea water. Fig. 4 shows the established experimental system.



261

262 **Fig. 4.** Diagram of experimental system: 1, Channel top (glass); 2, Seawater; 3, Copper base; 4,  
263 Helium inlet/outlet; 5, Anti-fog shell (b); 6, Seawater inlet; 7, Crystal observation unit; 8,  
264 Seawater outlet.

265 In the experimental study, the 31.8-ppt sea water of Qingdao city was used as the crystallisation  
266 solution. The experimental supercooling degree was -15 K. Because the single crystal will move  
267 along with the enforced flow, experiments were only designed for directional competition growth  
268 of sea ice crystals with or without the impact of both flow and heterogeneous particles. Iron particles  
269 (diameter at approximately 30  $\mu\text{m}$ ) were used as the heterogeneous particles. In order to prevent the  
270 influence of accidental error, 3 repeated experiments were carried out in each test. In the experiment,  
271 the temperature of the solution flowing into the field of view was -5  $^{\circ}\text{C}$ . The time interval for the  
272 control shooting was 3 s, the tip growth rate was calculated at intervals of 0.1 s, and the measurement  
273 was started after ice crystals wrapped the foreign particles. The experimental plan is listed in Table  
274 2. In addition, some related studies [48,49] have reported the characteristics of anisotropic  
275 morphology of ice crystals, which is a three-dimensional phenomenon. However, according to our  
276 experimental observation, if the crystallization occurs in a flat long rectangular channel and the  
277 thickness of the ice crystal channel is controlled within 0.01mm, the growth direction of the ice  
278 crystal is mainly parallel to the surface of the dendritic ice crystal, rather than the direction of the  
279 ice crystal thickness. Therefore, the ice crystal growth characteristics at this time can be  
280 characterized by 2D model, which can also be found in our previous research [29].

281

282 **Table. 2.** Experimental plan

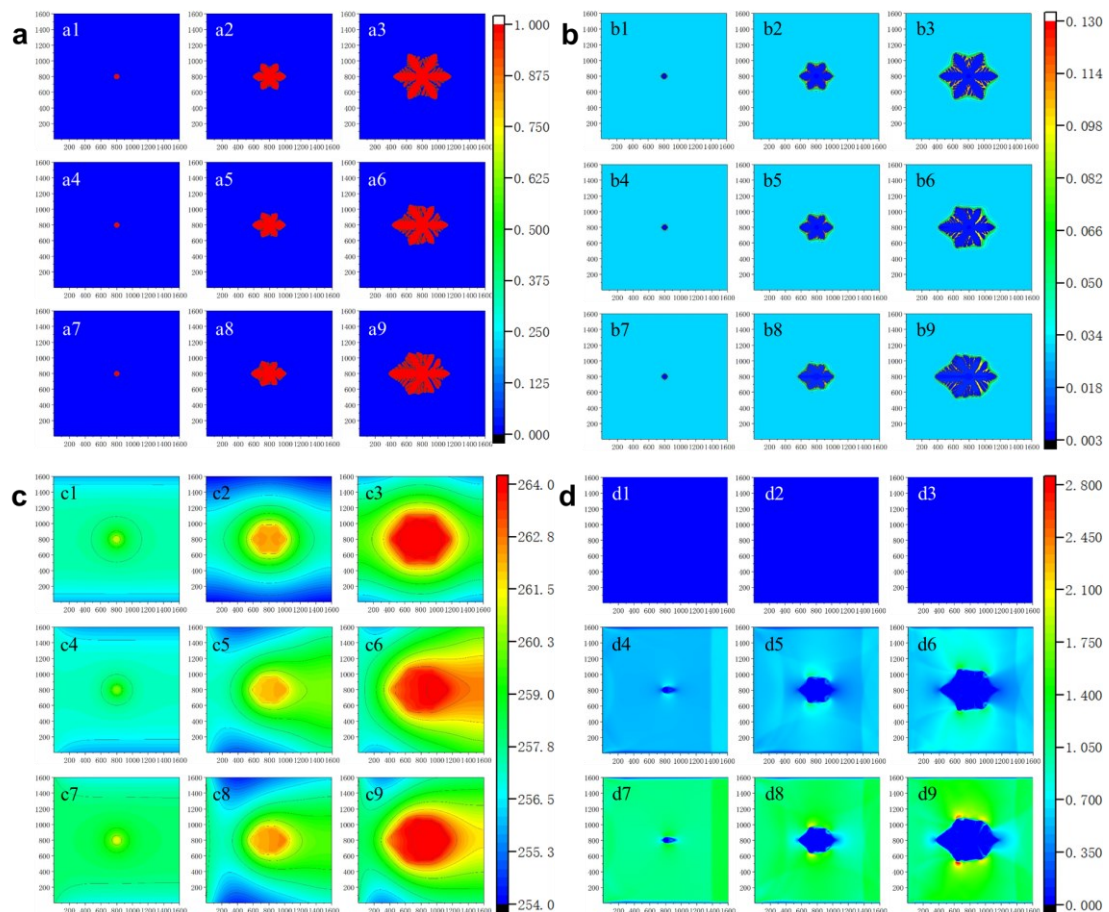
Experimental conditions	Flow velocity, m/s	Heterogeneous particles
Test 1	0	✓
Test 2	0	-
Test 3	0.025	✓
Test 4	0.025	-
Test 5	0.05	✓
Test 6	0.05	-

283

## 284 5 Results

285 In this section, both simulation and experimental results of the impact of flow and  
286 heterogeneous particles on the ice crystal growth process are presented. This section mainly focusses  
287 on the phenomenon presentation and discussion.

### 288 5.1 Impact of flow on sea ice crystals



289

290 **Fig. 5.** Simulation results of the phase, concentration, temperature, and velocity fields of the free

291 growth process of single sea ice crystal at different flow rates, where the initial subcooling degree of  
292 temperature is 15K, three velocity conditions are 0 m/s (no sea water flow), 0.5 m/s, and 1 m/s. a: the  
293 simulation results of the phase fields; b: the simulation results of the concentration fields; c: the  
294 simulation results of the temperature fields, d: the simulation results of the velocity fields;

295 Fig. 5 shows the phase, concentration, temperature, and velocity fields of the free growth  
296 process of single sea ice crystal at different flow rates. In each subfigure, the first, second, and third  
297 rows correspond to the simulation results of 0 m/s (no sea water flow), 0.5 m/s, and 1 m/s. Under  
298 the influence of ice crystal anisotropy [29], the crystal nucleus preferentially grows in the main axis  
299 dendrite in six directions, and then the secondary dendrite grows on the main axis dendrite. The  
300 secondary dendrites of different spindles appear in contact with the ice crystal pores [29]. The flow  
301 of sea water causes dendrites to grow asymmetrically. The length of the upstream spindle dendrite  
302 increased, the secondary dendrites were denser, and the downstream secondary dendrites were less  
303 numerous but thicker. The increase in flow velocity increased the asymmetry of ice crystals, the  
304 upstream spindle dendrite was longer and thicker, the number of secondary dendrites increased, the  
305 number of downstream secondary dendrites decreased, and the dendrite gap increased, which is  
306 beneficial for salt discharge. In addition, the related streamline diagrams in Fig 4(d1, d2, d3) are  
307 detailed presented in Appendix. A.

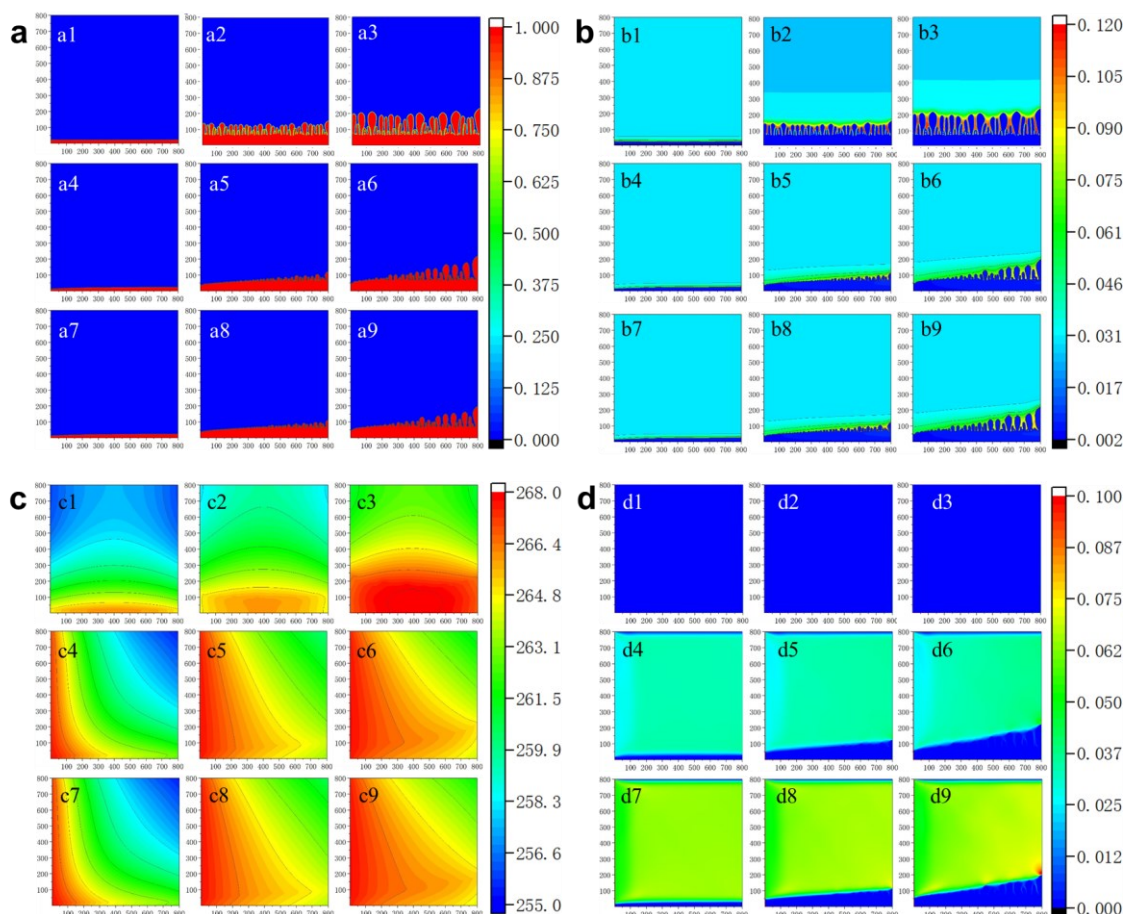
308 The salinity gradient at the tip of the spindle dendrite was greater than that at the tip of the  
309 secondary dendrite, which led to a greater growth rate of the spindle dendrite compared with the  
310 secondary dendrite. Solute enrichment was observed in the roots of the ice crystals. The sea water  
311 flow destroys the distribution of solutes. Upstream solutes accumulated downstream due to flow  
312 action [48]. The downstream [49] flow rate was low, and the salt was difficult to diffuse. The  
313 concentration gradient upstream of the ice crystal was greater than that downstream, and the growth  
314 rates on both sides of the ice crystal differed. A high flow rate promoted the diffusion of solutes. As  
315 the flow rate increased, the solute concentration gradient at the tip of the dendrite increased, which  
316 was beneficial for the growth of ice crystals.

317 The thermal diffusion layer at the tip of the main axis of the ice crystal was thinner, forming a  
318 larger temperature gradient. The latent heat of the solid phase continued to accumulate, and the  
319 latent heat at the root of the ice crystal diffused slowly, resulting in a thicker temperature diffusion



320 [50] layer at the root of the spindle and a reduced temperature gradient, which inhibited growth of  
321 the root. Furthermore, the flow promoted the latent heat transfer. The upstream latent heat was  
322 transferred downstream and superimposed with the downstream latent heat, resulting in a higher  
323 temperature gradient upstream than downstream. The heat transfer rate increased at high flow rates,  
324 and downstream heat accumulation decreased.

325 The upstream flow velocity of the dendrite was relatively high, while the downstream flow  
326 velocity was low, and wake vortex [51] appeared, which promoted solute diffusion and heat transfer.  
327 The velocity field became more complicated at high flow rates, and vortices appeared upstream.  
328 The high flow rate facilitated the discharge of salt in the dendrite gap, as well as the growth of ice  
329 crystals.



335 **Fig. 6.** Simulation results of the phase, concentration, temperature, and velocity fields of the directional  
336 competition growth process of sea ice crystals at different flow rates, where the initial subcooling  
337 degree of temperature is 15K, three velocity conditions are 0 m/s (no sea water flow), 0.025 m/s, and  
338 0.05 m/s, and the heat flux of bottom boundary is  $2 \times 10^5 \text{ J}/(\text{m}^2 \cdot \text{s})$ . a: the simulation results of the phase

339 fields; b: the simulation results of the concentration fields; c: the simulation results of the temperature  
340 fields; d: the simulation results of the velocity fields.

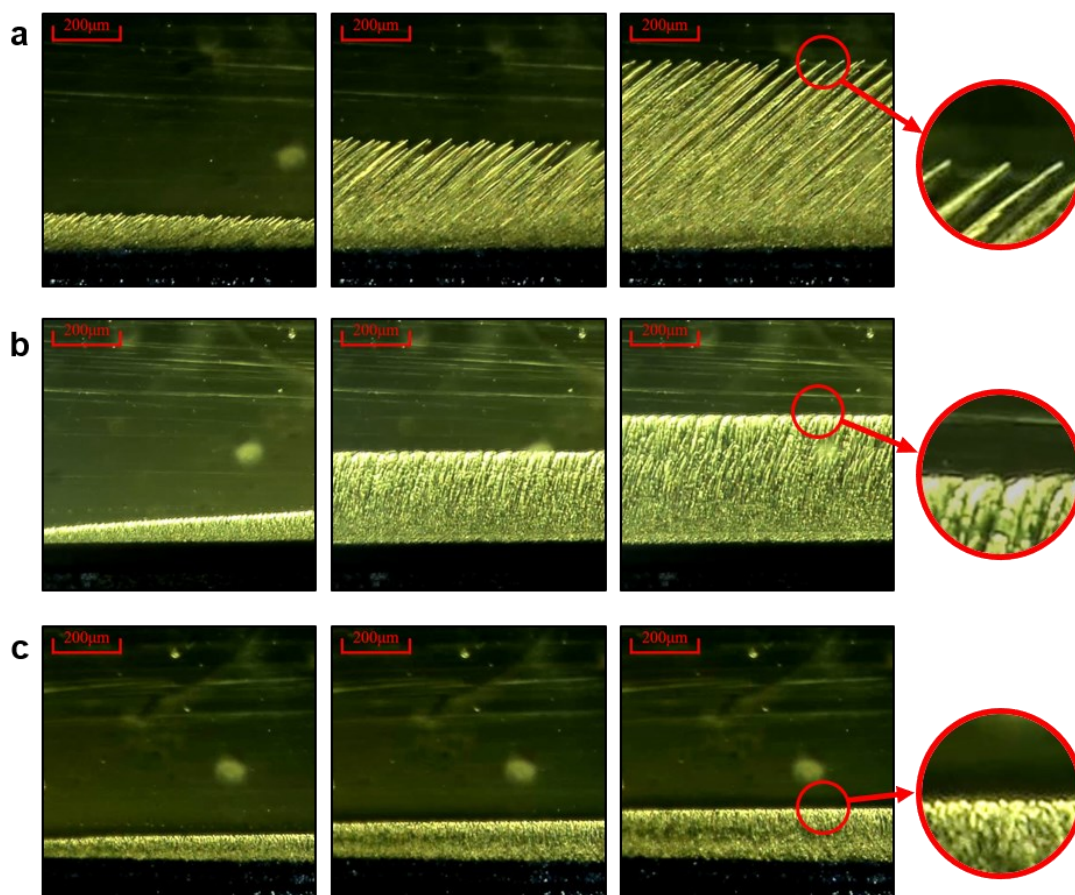
341 Fig. 6 shows the Simulation results of the phase, concentration, temperature, and velocity fields  
342 of the directional competition growth process of sea ice crystals at different flow rates. In each  
343 subfigure, the first, second, and third rows correspond to the simulation results of 0 m/s (no sea  
344 water flow), 0.025 m/s, and 0.05 m/s. It is found that the directional competitive growth of sea water  
345 can be divided into two stages. The first stage is uniform upward growth in the form of a plane. In  
346 the second stage, differentiated dendrites appear at the top of the plane crystal, demonstrating the  
347 competitive growth of multiple dendrites and limited growth of some dendrites. In the case of sea  
348 water flow, dendrite differentiation was delayed, and the dendrite was short and sparse. Affected by  
349 the temperature of the flowing sea water, the height of the ice crystal on the inlet side of sea water  
350 was lower than that on the outlet side of sea water. With an increase in the flow velocity, the dendrite  
351 height decreased, the dendrite became finer, the closure trend decreased, and the number of brine  
352 pockets decreased. In addition, the related streamline diagrams in Fig 5(d1, d2, d3) are detailed  
353 presented in Appendix. A.

354 The solute field was evenly distributed in the plane crystal stage. During the growth stage of  
355 dendrite differentiation, a high concentration of brine pockets discharged from the growth of ice  
356 crystals gathered between the dendrites, and the concentration between the dendrites continued to  
357 rise, inhibiting the growth of the bottom dendrites, indicating that the dendrite bottom is slender and  
358 the top is thick. The flow of sea water promoted the diffusion of solutes, while the concentration of  
359 solutes between dendrites was low, and the concentration gradient was small. With a higher flow  
360 rate, this effect became more apparent.

361 The change in the temperature field in the case of no flow was mainly due to the co-action of  
362 latent heat and bottom heat flux. The latent heat of crystallisation accumulated at the tip of the ice  
363 crystals, and the degree of supercooling decreased, which inhibited the growth of ice crystals.  
364 Because the temperature of the flowing sea water was higher than that of the original sea water, the  
365 latent heat and heat of the flowing sea water were superimposed, resulting in a temperature peak  
366 trend, which greatly reduced the tip supercooling.

367 The inlet ice crystals of the sea water were thin, the flow area was large, and the ice layer in

368 the outlet area was thicker, compressing the flow space of the sea water. In addition, the flow  
369 velocity of the sea water showed an upward trend. A slower flow rate was exhibited at the tip of the  
370 ice crystal, and the solution between the dendrites presented a micro-flow situation. The flow  
371 between dendrites became more obvious, and hence promoted the transfer of the solute and the  
372 diffusion of heat.



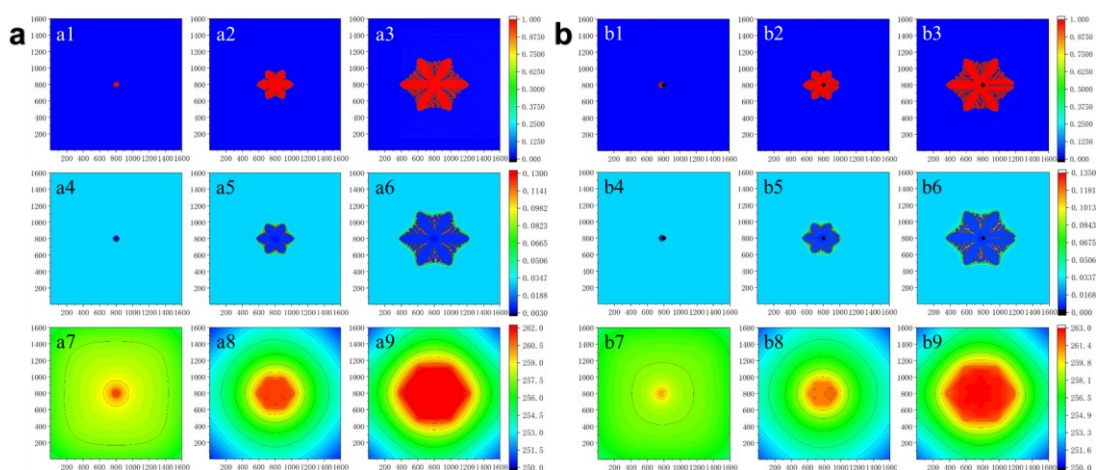
373  
374 **Fig. 7.** Experimental verification of the directional competition growth process of sea ice crystals  
375 for velocities of a: 0 m/s; b: 0.025 m/s; c: 0.05 m/s, where the supercooling degree is -15 K.

376 Fig. 7 shows the experimental results of the directional competition growth process of sea ice  
377 crystals with the impact of flow. In order to prevent the influence of accidental error, 3 repeated  
378 experiments were carried out, and one group was selected and analysed. The results show that at the  
379 flow rate of 0 m/s, sea water-oriented crystallised dendrites had finer tips, and the saltwater channels  
380 between dendrites were thicker. At the flow rate of 0.025 m/s, the tip of the ice crystals was smooth,  
381 and the brine channel narrowed, showing a shrinking trend. The tip of the ice crystal at the flow rate  
382 of 0.05 m/s was extremely small, and the brine channel was dense. Meanwhile, the ice crystal growth

383 rate was fastest at the flow rate of 0 m/s, followed by that at 0.025 m/s, and slowest at 0.05 m/s,  
384 which is consistent with the simulation results.

### 385 5.2 Impact of heterogeneous particle on sea ice crystals

386 This part describes the simulations, experiments, and analysis of the influence of heterogeneous  
387 particle [52] on the growth of ice crystals. The crystallisation situations of ice single-crystal free  
388 growth and directional competition growth were simulated. The program iterated 2,000 steps and  
389 recorded the results of the ice crystal growth once.



390  
391 **Fig. 8.** Comparison of simulation results of ice single-crystal free growth under a: homogeneous  
392 nucleation; b: influence of heterogeneous particles, where the initial subcooling degree of temperature  
393 is 15K.

394 The simulation results of single sea ice crystal growth are shown in Fig. 8. In each subfigure,  
395 the first, second, and third rows display the simulation results of the phase, concentration, and  
396 temperature fields, respectively.

397 In the homogeneous nucleation condition, the location of the circular initial crystal nucleus was  
398 set in the centre of the simulation area with the diameter of  $10dx$ . For the influence of heterogeneous  
399 particles, the heterogeneous particles were located in the centre of the simulation area with the  
400 diameter of  $10dx$ , the initial crystal nucleus centre was located on the left side of the heterogeneous  
401 particles with the radius of  $10dx$ , and the contact angle was  $90^\circ$ .

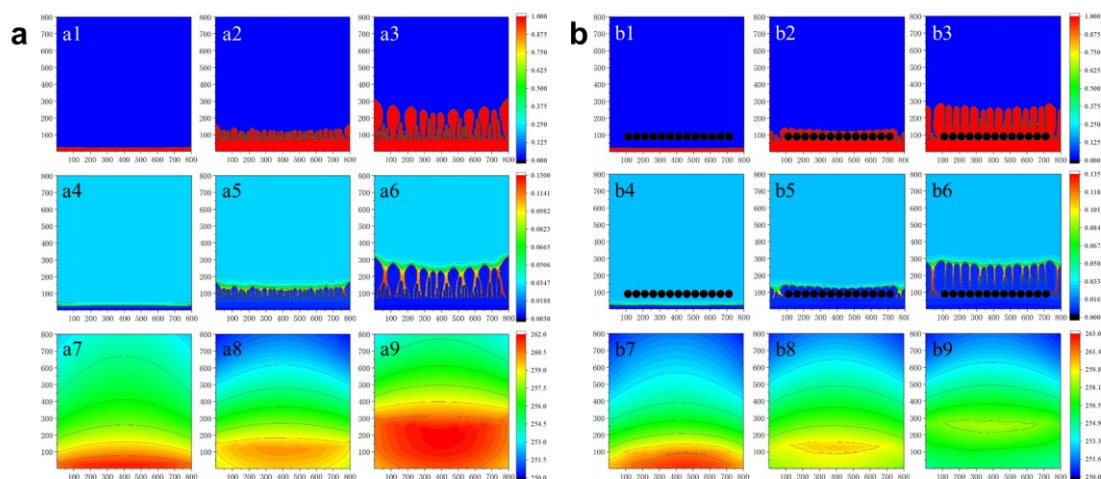
402 In the phase field, the phase-field value of the heterogeneous particles was set to -1, the liquid  
403 phase part of sea water was 0, the solid phase part was 1, and the solid-liquid interface had a value  
404 between 0 and 1. Ice crystals preferentially encapsulated heterogeneous particles during the initial



405 growth process. Affected by anisotropy, the growth of the ice crystal nuclei was hexagonal, but there  
 406 was no apparent dendrite differentiation. Because the initial crystal nucleus was located on the left  
 407 side of the heterogeneous particles, a gap appeared in the right side of the ice crystal when the  
 408 heterogeneous particles were wrapped. Under heterogeneous nucleation conditions [53], the gap  
 409 between the main and secondary dendrites of ice crystals was larger than that under homogeneous  
 410 nucleation. This increase in voids helped the discharge of high-concentration solutions, reduced the  
 411 number of brine pockets, and reduced the probability of small brine formation.

412 The concentration field in the presence of heterogeneous particles is basically the same as that  
 413 in the absence of particles [54]. At the location where the ice crystals are close to the right side of  
 414 the particle, there was a significant increase in the solute concentration. The salt removal rate was  
 415 greater than the solute diffusion rate, which led to the accumulation of high-concentration sea water  
 416 and inhibited the closure of ice crystals.

417 Moreover, the release of latent heat of crystallisation caused the temperature of the ice crystal  
 418 centre and the temperature of the heterogeneous particles to rise. The thermal conductivity of the  
 419 heterogeneous particles is much greater than that of the ice crystals. The supercooling degree of the  
 420 closed position of the ice crystal is affected by the temperature of the heterogeneous particles and  
 421 the latent heat of sea ice crystallisation. The supercooling degree was too large, which promoted the  
 422 growth of the ice crystals to a certain extent.



423  
 424 **Fig. 9.** Comparison of simulation results of the directional competition growth of sea ice crystals under  
 425 a: homogeneous nucleation; b: influence of heterogeneous particles, where the initial subcooling degree  
 426 of temperature is 15K, and the heat flux of bottom boundary is  $2 \times 10^5 \text{ J}/(\text{m}^2 \cdot \text{s})$ .

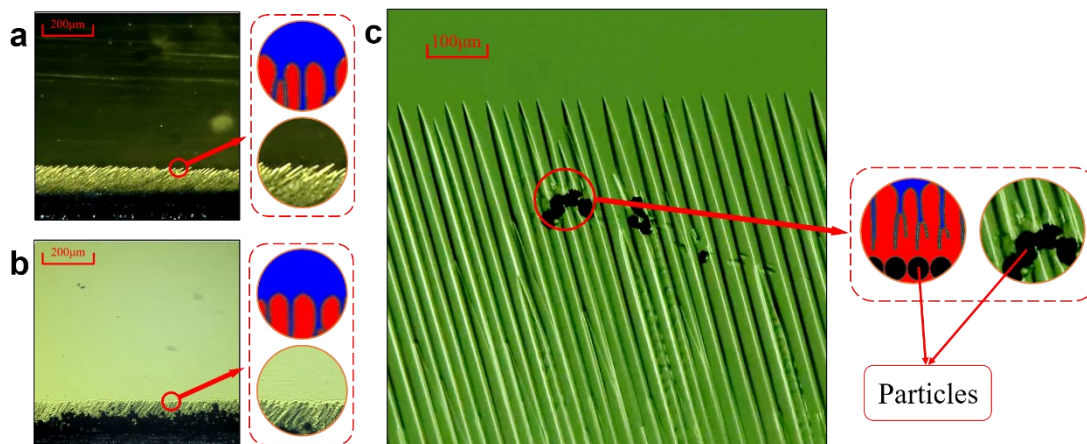
427 Fig. 9 shows the simulation results of directional competition sea ice crystal growth. In each  
428 subfigure, the first, second, and third rows correspond to the simulation results of the phase,  
429 concentration, and temperature fields. It is found that the directional competition growth process of  
430 sea ice crystals with and without heterogeneous particles was simulated. The heterogeneous  
431 particles were uniformly arranged at the height of  $100dy$  with the diameter of  $40dx$ , and the centre  
432 spacing of different heterogeneous particles was  $100dx$ . The initial crystal nucleus was located at  
433 the bottom of the simulation area with the length of  $800dx$  and height of  $5dx$ .

434 The initial growth process of ice crystals was not affected by the heterogeneous particles and  
435 formed flat crystals, similar to homogeneous nucleation. When the ice crystals contacted the  
436 heterogeneous particles at 5,000 steps, the growth rate significantly increased. Ice crystals  
437 preferentially encapsulated heterogeneous particles, and dendrites began to differentiate after being  
438 completely encapsulated, forming saltwater channels. Thus, a relationship exists between  
439 heterogeneous particles and ice crystal dendrites. When heterogeneous particles were present, the  
440 morphology of ice crystals was more orderly, the dendrites thickened, the brine channels were  
441 thinner, the ice crystals grew denser, and the brine pockets at the bottom were clearly reduced.

442 After the ice crystals contacted the foreign particles, the regions of the foreign particles did not  
443 generate high concentrations of brine pockets. There were high-concentration sea water channels on  
444 both sides of the heterogeneous particle area. With the growth of ice crystals, high-concentration  
445 brine channels formed above the heterogeneous particles, and the concentration was significantly  
446 higher than that under homogeneous nucleation conditions. The presence of high-concentration  
447 brine in the channel inhibited the growth of ice crystals, hence growth of the secondary dendrites of  
448 this part of the ice crystals became difficult, and the probability of forming brine pockets greatly  
449 reduced.

450 The change in the temperature field in the presence of heterogeneous particles is basically  
451 consistent with that under homogeneous nucleation, and the highest temperature was located at the  
452 tip of the directional-growth ice crystal. Initially, the bottom heat flux dissipated the latent heat of  
453 crystallisation, but as the ice crystals gradually grew, the released latent heat gradually accumulated,  
454 causing the temperature of the ice crystal tip to first rise and then drop. Because the thermal  
455 conductivity of the heterogeneous particles is better than that of ice crystals, the heat transfer is

456 faster than that of homogeneous nucleation, and the degree of supercooling of the ice crystals around  
457 the heterogeneous particles decreased, so that the crystallisation increased and stabilised.



458

459 **Fig. 10.** Comparison of experimental and simulation results of directional competitive growth of ice  
460 crystals under different conditions of a: without foreign particles; b: under the influence of  
461 heterogeneous particles, located at the bottom of the crystallisation area; c: influence of free  
462 heterogeneous particles on the directional growth of ice crystal dendrites.

463 Fig. 10 shows the comparison of experimental and simulation results of directional competitive  
464 growth of ice crystals under different conditions. Enlarged parts show the details of the tips of the  
465 ice crystals compared with the simulation results. In order to prevent the influence of accidental  
466 error, 3 repeated experiments were carried out. Experimental results of directional competitive  
467 growth of ice crystals:

468 By comparing Fig. 10a and b, the growth state of ice crystals under multi-particle conditions  
469 at the bottom is basically the same as that without particles. In the absence of heterogeneous particles,  
470 the dendrites appeared slender, the mutual inhibition between the dendrites was serious, and the  
471 dominant dendrite growth position was clear. Meanwhile, in the presence of heterogeneous particles  
472 at the bottom, the tip of the directional growth of ice crystals was relatively smooth, the tip dendrites  
473 were larger, and the dendrites were thicker. The growth heights of different dendrites were basically  
474 the same, there was no apparent dendrite inhibition, and the brine channel between the dendrites  
475 was narrow, which is basically in line with the results of the simulation.

476 As can be seen in Fig. 10c, the tip of the ice crystal presented a homogeneous nucleation ice  
477 crystal directional competition growth state before contacting the heterogeneous particles. After

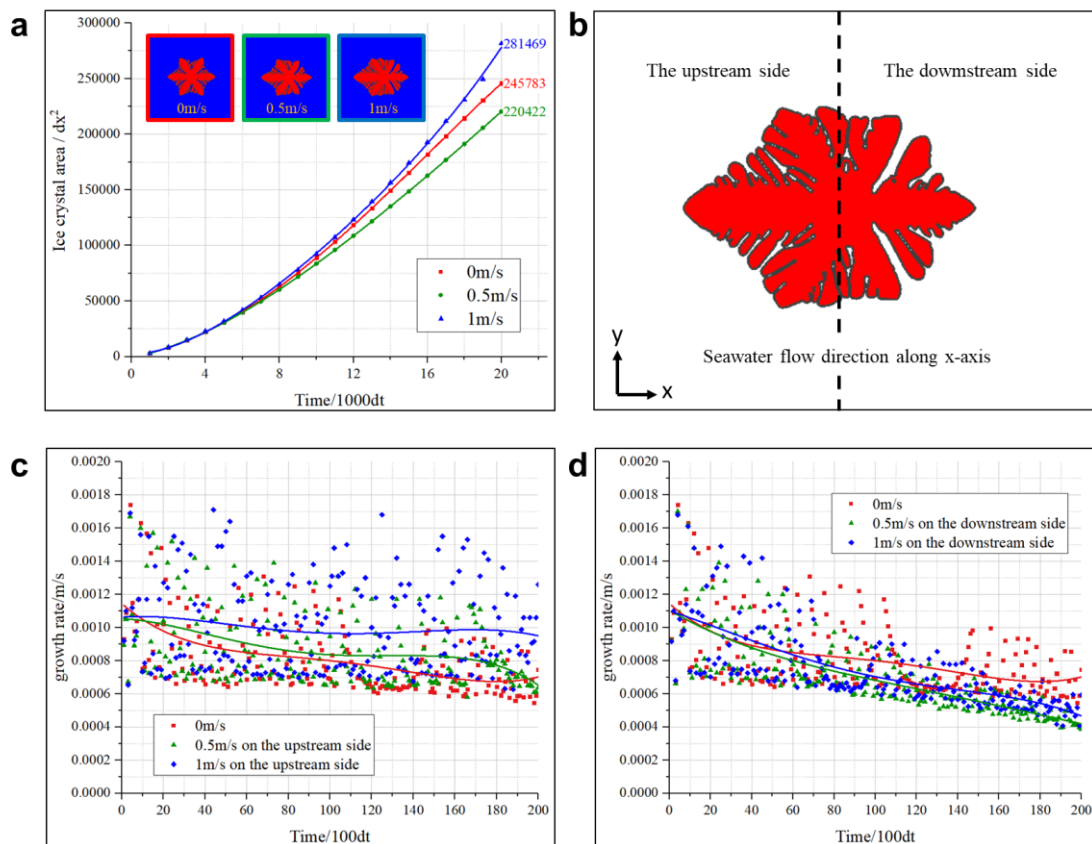
478 contacting the foreign particles, the foreign particles were wrapped, and then the dendrites grew  
479 outward. In addition, the dendrites were thicker than before the wrapping. Dendrites exhibited  
480 secondary dendrite differentiation as the brine channel narrowed.

## 481 6 Discussion

482 In this section, the influences of flow and heterogeneous particles on the ice crystal growth  
483 process are discussed. Each discussion includes two parts: data analysis via simulation and data  
484 processing results from the experiment. The main data parameters analysed were the ice crystal area,  
485 ice crystal tip growth rate, bottom heat flux change, and dendrite diameter.

### 486 6.1 Impact of sea water flow on the growth of ice crystals

487 The area and growth rate of ice crystals in the simulation were analysed, and the bottom heat  
488 flux density and tip growth rate were recorded and processed. The parameters of the ice crystal area  
489 and ice crystal tip growth rate were selected for analysis. In the program, the ice crystal area was  
490 calculated every 1,000 steps, and the ice crystal tip growth rate was calculated every 100 steps. The  
491 speed calculation results were analysed using equation fitting to form a growth speed fitting curve.



492  
493 **Fig. 11.** Analysis of the simulation results of the free growth of ice single-crystals at different flow rates



494 of a: ice crystal area curve at different flow rates; b: diagram of ice crystal; c: ice crystal upstream  
495 growth rate and velocity fitting curve at different flow rates; d: ice crystal downstream growth rate and  
496 velocity fitting curve at different flow rates.

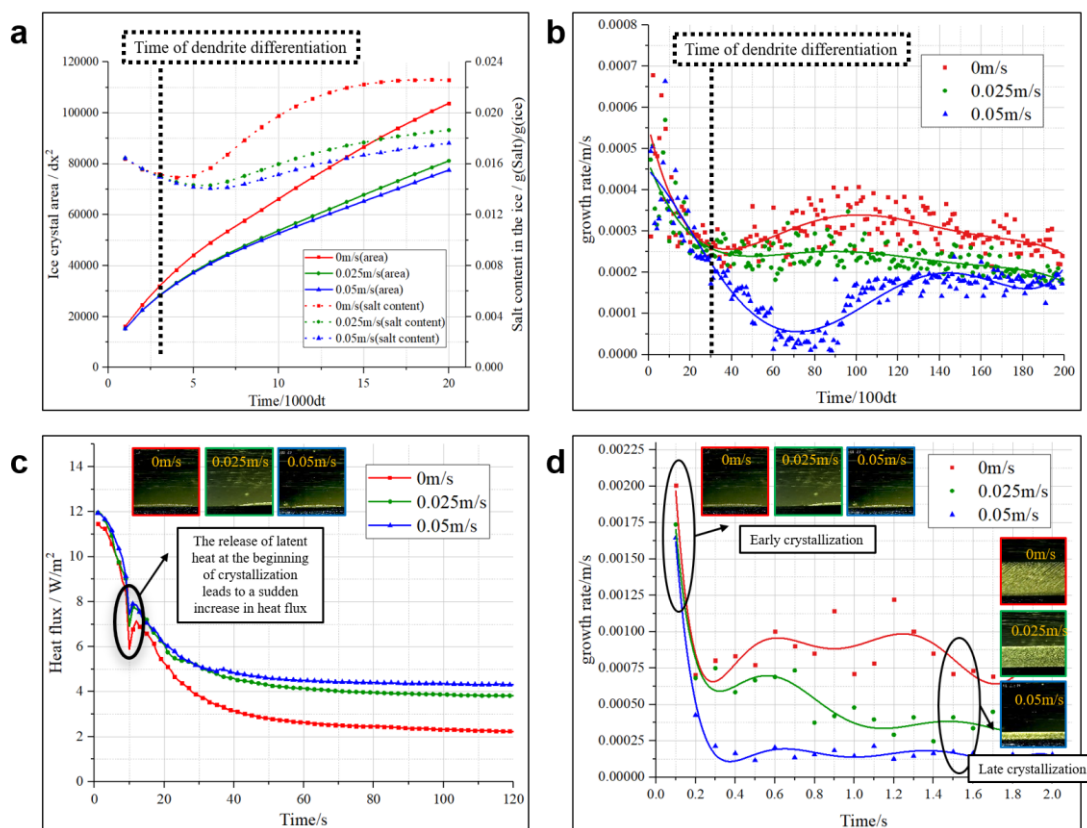
497 Fig. 11 shows the simulation results of the free growth of ice single-crystals at different flow  
498 rates. The ice crystal area is based on the grid length ( $dx$ ), and the unit area is expressed as  $dx^2$ . The  
499 ice single-crystal area is largest when the flow rate is 1 m/s, followed by that when the sea water is  
500 still, and smallest when the flow rate is 0.5 m/s. The difference in the ice crystal area under high and  
501 low flow rates is approximately 20%. In the upstream, the ice crystal tip growth rate is largest when  
502 the flow velocity is 1 m/s, followed by that when the flow velocity is 0.5 m/s, and smallest when  
503 the sea water is still. In the downstream, the ice crystal tip growth rate is the highest when the sea  
504 water is stationary, followed by that when the flow velocity is 1 m/s, and smallest when the flow  
505 velocity is 0.5 m/s.

506 From the area of ice single-crystals under static sea water, a low flow rate inhibits the growth  
507 of single crystals, while a faster flow rate is beneficial to the growth of the ice single-crystal. The  
508 ice crystal area under static sea water is 14.5% less than that at 1 m/s, and 10.3% more than that at  
509 0.5 m/s. Comparing the growth rate of the upstream and downstream sides, the flow of sea water  
510 can promote the growth of the upstream ice crystals, while the downstream ice crystal growth is  
511 inhibited. The different growth conditions on both sides of the ice crystals also explain the difference  
512 in the area of ice crystals at different flow rates.

513 Upstream, the growth rate of ice crystals increased by 15%-30%, and the effect of flow on ice  
514 crystal growth is mainly reflected in promotion of the diffusion of latent heat and solute. The ice  
515 crystal tip temperature gradient and solute concentration gradient were large, and the growth rate  
516 was stable. Downstream, the growth rate of ice crystal decreases about 10%-20%, and the effect of  
517 sea water flow on the diffusion of latent heat and solutes remained, but will transfer the latent heat  
518 and solutes from the upstream to the downstream, causing accumulations of the latent heat and  
519 solutes, which inhibit the growth of ice crystals. With an increase in the number of iteration steps,  
520 the latent heat and solute increased, and the diffusion effect of flow on the latent heat and solute  
521 remained stable, resulting in a downward trend in the growth rate of the downstream ice crystal tip.

522 Upstream, the higher the flow rate, the better the growth of the ice crystals. Whereas,

523 downstream, owing to the accumulation and diffusion caused by flow, the diffusion effect of lower  
524 flow velocity was weaker than the accumulation effect, which inhibits the growth of ice crystals. As  
525 the flow rate increased, the diffusion effect gradually strengthened, and the downstream ice crystal  
526 growth rate gradually increased. In general, with the increase in the flow velocity, the downstream  
527 ice crystal growth rate shows a trend of first declining and then increasing, which also explains the  
528 reason for the smallest ice crystal area in the case of 0.5 m/s in the simulation.



529  
530 **Fig. 12.** Simulation and experimental data analyses of the directional competitive growth of ice crystals  
531 at different flow rates of a: growth trend of ice crystal area (simulation); b: trend of the tip growth rate  
532 (simulation); c: heat flux change at the bottom of the crystallizer (experiment); d: changing trend of the  
533 tip growth rate (experiment).

534 As is shown in Fig. 12a, the ice crystal area is based on the grid length ( $\text{dx}$ ), and the unit area  
535 is expressed as  $\text{dx}^2$ . The area of ice crystals grown by directional competition in stationary sea water  
536 is larger than that in the case of sea water flow by approximately 25%. Compared with the ice crystal  
537 area under static sea water, the ice crystal area decreased by 21.8% at 0.025 m/s and 25.3% at 0.05  
538 m/s. The heat generated by sea water is a key factor affecting the growth of ice crystals. Regarding  
539 the area growth trend, the area of ice crystals grown by directional competition in sea water in the

540 static state increased much faster than that in the presence of sea water flow. The ice crystal area  
541 growth at the flow rate of 0.025 m/s was slightly faster than that at 0.05 m/s, but the overall  
542 difference is not significant.

543 According to Fig. 12b, in the first 3,000 steps of ice crystal growth, the ice crystals grew in the  
544 form of planar crystals. The growth rates of the ice crystal tips in the three cases were relatively  
545 scattered, and no difference was exhibited. In the initial stage of directional competitive growth of  
546 ice crystals, owing to the small amount of crystallisation, the release of latent heat was low, and the  
547 flow of sea water had less influence on the ice crystals. In approximately 3,000 steps, the ice crystals  
548 began to differentiate. A higher flow rate reduced the supercooling of the ice crystal tip. Although a  
549 higher flow rate can remove the latent heat released by the ice crystal and promote the transfer of  
550 solute, owing to the influence of the heat of the flowing sea water, the growth of the ice crystal is  
551 always inhibited. With an increase in the number of iteration steps, the effect of the bottom heat flux  
552 again became apparent, and the growth rate of the ice crystal tip appeared to increase; finally, it  
553 reached a dynamic balance with the latent heat of crystallisation and the heat of flowing sea water.  
554 In general, under simulated conditions, the growth rate of ice crystals under static conditions is  
555 always greater than that in the presence of flow.

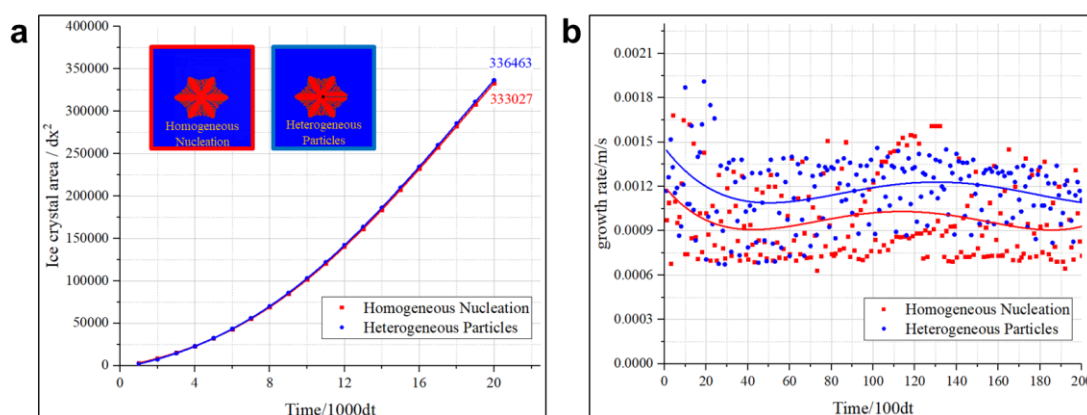
556 Fig. 12c shows the heat flux change during crystallisation. It is found the change in heat flux  
557 caused by the temperature difference between the bottom of the crystallizer and the wall of the  
558 refrigerating plate was measured during the crystallisation process in the experiments. The initial  
559 temperature of sea water was higher than the wall temperature, and the heat flux in the figure shows  
560 a downward trend. At 10 s, the sea water began to crystallise, and the latent heat of crystallisation  
561 released caused the heat flux density to suddenly rise. As time increased, the temperature difference  
562 between the cold wall surface and crystallizer gradually decreased, and the heat flux density  
563 decreased slowly. In the case of sea water flow, the value of the crystallisation heat flux caused by  
564 the heat generated by the sea water was stable, compared with the case of static sea water. At a  
565 higher flow rate, more heat is transferred by the sea water, resulting in differences in the heat flux  
566 density at different flow rates.

567 Fig. 12d shows that under the experimental conditions, owing to the influence of the heat flux  
568 on the bottom surface, the ice crystal growth rate under the three flow rates was extremely fast in

569 the initial stage of ice crystal growth, but the duration was very short. With the increase in time, the  
570 growth rates of ice crystals under the three flow rates showed a steady state of fluctuation. The heat  
571 from the flowing sea water caused a difference in the growth rate of ice crystals under the three  
572 conditions. The growth rate at the flow rate of 0.05 m/s was lowest and the most stable.

## 573 6.2 Impact of homogeneous particles on the growth of ice crystals

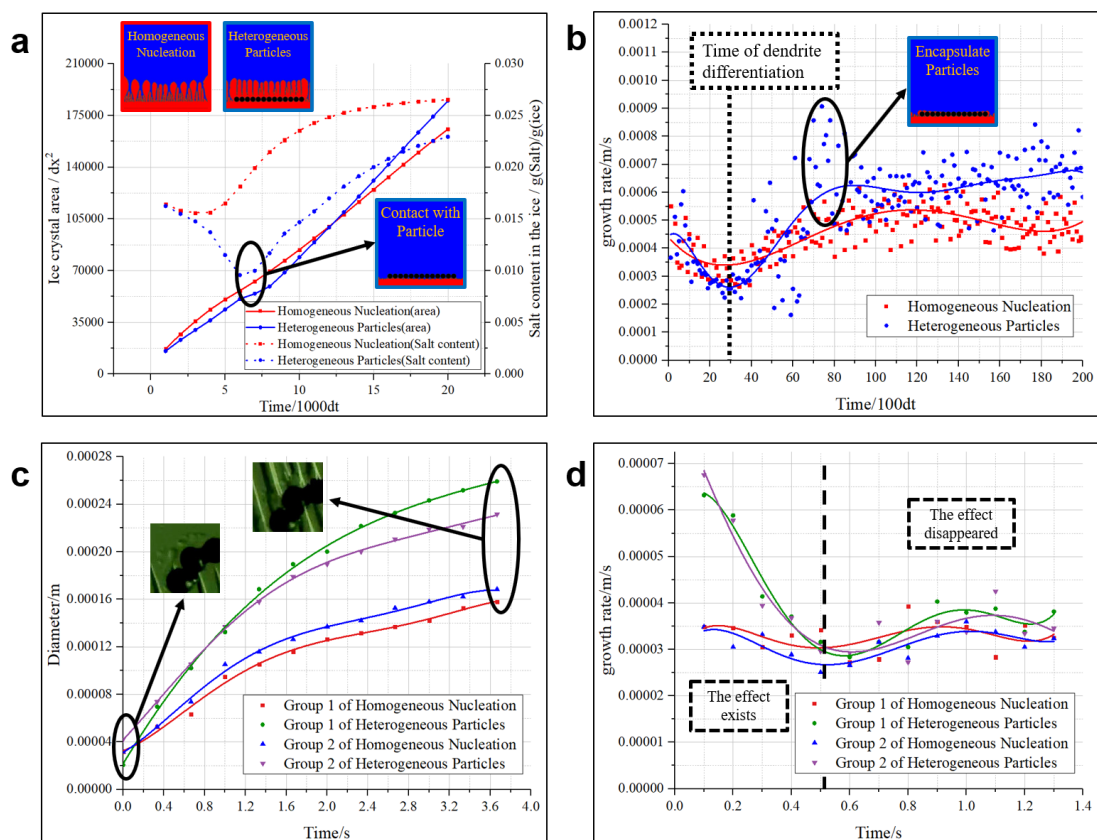
574 In this section, the area and growth rate of ice crystals in the simulation were analysed, and the  
575 ice crystal dendrite diameter and tip growth rate in the experiment were recorded and processed.  
576 The selection of the calculation points was consistent with that in the flow state.



577

578 **Fig. 13.** Analysis of the simulation results of ice crystal area and tip growth rate of ice single-crystal  
579 free growth in homogeneous nucleation conditions and under the influence of heterogeneous particles  
580 of a: ice crystal area; b: ice crystal growth rate.

581 Fig. 13 shows the simulation results comparison of single sea ice crystal with different  
582 nucleation methods. Although the nucleation stage provides the most fundamental manifestation of  
583 the different nucleation methods, it is found do not have a significant influence on the area of free  
584 growth of ice single-crystals. Single-crystal free growth, homogeneous nucleation, and  
585 heterogeneous nucleation exhibited basically the same change trend for the ice crystal tip growth  
586 rate; relatively fast at the beginning and then generally stable. From the numerical analysis, because  
587 the thermal properties of heterogeneous particles are better than those of ice crystals, the tip growth  
588 rate of ice crystals in the presence of heterogeneous particles is always higher than that in the case  
589 of homogeneous nucleation. However, the difference in the area of the ice crystals between the two  
590 cases is not large, indicating that the gap between the dendrites of the ice crystals is larger in the  
591 case of heterogeneous nucleation, which is consistent with the results of the simulation.



592

593 **Fig. 14.** Simulation and experimental data analyses of the directional competitive growth of sea ice  
 594 crystals in homogeneous nucleation conditions and under the influence of heterogeneous particles of a:  
 595 simulated ice crystal area (simulation); b: simulated ice crystal growth rate (simulation); c:  
 596 experimental dendrite tip diameter (experiment); d: experimental ice crystal growth rate (experiment).

597 Fig. 14 shows the simulation and experimental results comparison of directional competitive  
 598 growth of sea ice crystals with or without the impact of homogeneous particles. As is shown in Fig.  
 599 14a, in the initial stage of crystallisation, the area of ice crystals under homogeneous nucleation  
 600 conditions was larger than that under heterogeneous particles. At approximately 7,000 steps, the  
 601 growth rate of the ice crystal area under the condition of heterogeneous particles was greater than  
 602 that under the condition of homogeneous nucleation. This is the time at which ice crystals  
 603 completely enveloped the heterogeneous particles. In the presence of heterogeneous particles, the  
 604 ice crystal area at 20,000 steps was 10.8% larger than that under homogeneous nucleation conditions.  
 605 Thus, heterogeneous particles can promote an increase in the ice crystal area to a certain extent.  
 606 Furthermore, the simulation results show that heterogeneous particles can reduce the salt residue in  
 607 ice crystals. In the presence of heterogeneous particles, the concentration of ice crystal salt first

608 decreases and then increases. When the ice crystal contacts with heterogeneous particles, the salt  
609 content in the ice reaches the lowest, which is about 48% lower than that in homogeneous nucleation  
610 conditions. With the increase of time, the salt content in the ice increases slowly. After the 20000-  
611 step iteration, the ice crystal salt content difference between the two cases is about 14.8%.

612 It is found in Fig. 14b that during the growth period of planar crystals, the growth rates of ice  
613 crystals under the two nucleation conditions exhibited downward trends, reaching the lowest at  
614 3,000 steps, and then showed a steady increasing trend. Under the condition of heterogeneous  
615 particles, the growth rate of ice crystals in the initial stage of ice crystal growth declined significantly  
616 faster than that under homogeneous nucleation conditions. After reaching the lowest speed, the  
617 growth rate was also significantly higher than that of ice crystals under homogeneous nucleation  
618 conditions. At approximately 5,000 steps, ice crystals started to contact the heterogeneous particles,  
619 and the growth rate exceeded and remained greater than that under homogeneous nucleation  
620 conditions. At approximately 7,000 steps, the ice crystals enveloped the heterogeneous particles,  
621 and the ice crystal growth rate appeared at a maximum. Because the thermal conductivity of  
622 heterogeneous particles is better than that of ice crystals, the latent heat released by the growth of  
623 ice crystals and bottom heat flux acted on the heterogeneous particles, causing the temperature  
624 change of the heterogeneous particles to be greater than that of the ice crystal, and leading to a sharp  
625 change in the growth rate of ice crystals.

626 According to Fig. 14c, in the initial growth stage of ice crystals, the growth rate of dendrite  
627 diameter was faster than that of dendrites without heterogeneous particles. because the thermal  
628 conductivity of heterogeneous particles is better than that of sea ice crystals, the temperature reduced  
629 around the heterogeneous particles. Meanwhile, the existence of heterogeneous particles disturbed  
630 the stability of the original free energy, and the interface free energy at the boundary changed  
631 suddenly, which promoted crystallisation. After the ice crystals completely encapsulated the  
632 heterogeneous particles, the growths of the ice crystals under the two conditions again tended to be  
633 the same; as a result, after 2 s, the dendrite growth rates under the two conditions gradually  
634 approached on another, and the change rate of diameter with time was basically the same.

635 As is shown in Fig. 14d, the existence of heterogeneous particles changed the supercooling and  
636 free energy distribution at the tip of the ice crystals. With the increase in time, the ice crystals

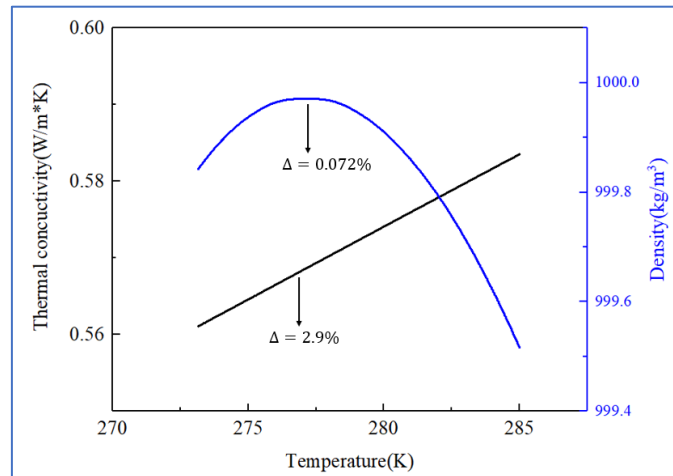
637 continued to grow, and the influence of heterogeneous particles gradually decreased. The growth  
638 rate of ice crystal tips exhibited a trend of first decreasing and then stabilising. Whereas, in the  
639 absence of heterogeneous particles, the growth rate of the ice crystal tip showed a dynamic and  
640 stable trend. The values of the ice crystal tip growth rates under the two conditions were similar  
641 after stabilisation, indicating that the effect of heterogeneous particles on the growth of ice crystals  
642 is mainly concentrated on the ice crystal.

## 643 **7 Conclusions**

644 This study provides a methodology of numerically simulate sea ice crystallisation which  
645 includes the phase change, solute migration, heat transfer and flow, as well as a feasible controlling  
646 approach to improve desalination efficiency of sea water frozen crystallisation. Both the single sea  
647 ice crystallisation which reflects the suspension freeze crystallisation and the directional competitive  
648 sea ice crystallisation which reflects the layer freeze crystallisation were investigated. A four-  
649 physical-fields coupling model for sea ice crystallisation was established to conduct the simulation,  
650 a high-definition 3D transmission microscope observation experimental system was built up to  
651 experimental verify the simulation results. Sea ice crystal morphology, solute diffusion, and heat  
652 flux changes during the crystallisation process were investigated. The results show the potential for  
653 reducing salt residues and increasing ice crystal production during sea water freezing. Main  
654 conclusions are made as follows:

- 655 1) The flow of sea water results in the formation of different concentrations and temperature  
656 gradients, which promotes the diffusion of discharged salt and the growth of ice crystals,  
657 and reduces the probability of dendrite closure.
- 658 2) In the directional competitive growth of ice crystals, the salt content in the ice decreased  
659 by 17.4% at 0.025 m/s and 21.9% at 0.05 m/s, respectively, although the ice crystal area  
660 decreased by 21.8% at 0.025 m/s and 25.3% at 0.05 m/s, respectively.
- 661 3) The existence of heterogeneous particles can narrow the brine channel, increase the growth  
662 rate and the area of ice crystals.
- 663 4) In the directional competitive growth of ice crystals under the condition of heterogeneous  
664 particles, the ice crystal area increased by 10.8% and the trapped salt content in the ice  
665 crystals decreased by 14.8%.

666 **Appendix A**

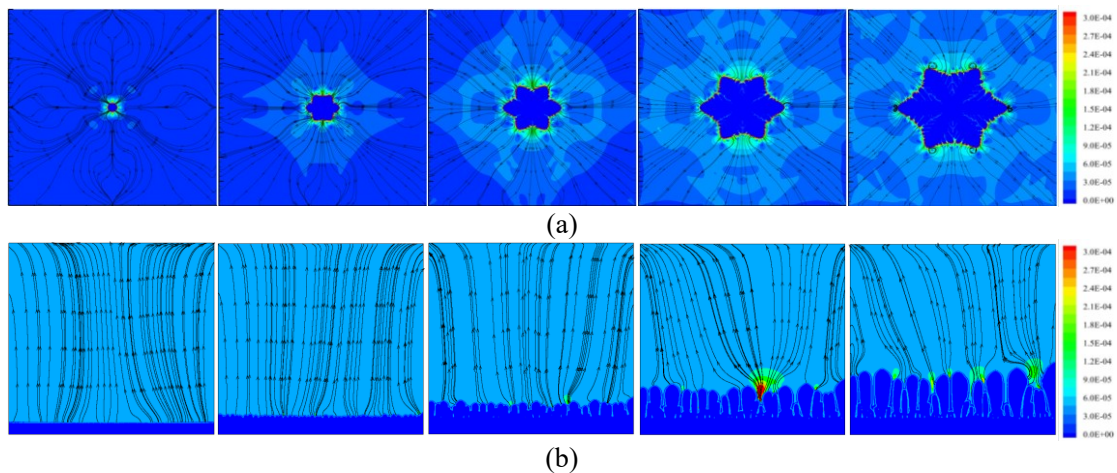


667

668 Fig. 15. Thermophysical properties of seawater

669 **Appendix B**

670 The velocity field of single and directional sea ice crystallisation are detailed presented in Fig.  
 671 16(a) as the supplementary to Fig. 6 (d1, d2, d3), and Fig. 16(b) as the supplementary to Fig. 7 (d1,  
 672 d2, d3), respectively.



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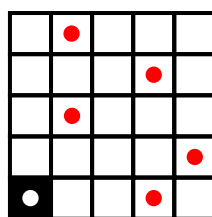
677 **Fig. 16.** Natural convection velocity field during sea ice crystallisation: (a) single crystallisation;  
 678 (b) directional crystallisation

679 **Appendix C**

680 The compiled C++ program involves coupling solution of multiple field based on different  
 681 algorithms, and the complication of calculation and data calling results in low simulation efficiency.  
 682 In order to solve this problem, an adaptive optimization algorithm is proposed. It is worth noting  
 683 that the numerical values of grids are not always affected by crystallisation during ice crystal growth,



684 once the grid values remain unchanged, calculation on this part of the grids is jumped. The schematic  
685 diagram of optimization algorithm is shown in Fig. 17 and described as follows: firstly, build a  $5 \times$   
686  $5$  block next to the boundary grid (shown on the bottom left); secondly, randomly select another 5  
687 calculated grids in the block; thirdly, calculate the phase-field parameter and concentration gradient  
688 between these grids, once the gradient of phase-field parameter and concentration are less than a  
689 small value, it can be considered that the parameters within this block is uniform, therefore the entire  
690 block is deemed as a new real-time adaptive upgrading grid.



691

692 **Fig. 17.** Schematic diagram of adaptive optimization algorithm

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## 821 **Author contributions**

822 J. S. completed the preparation of the simulation program, designed and conducted experiments,  
823 completed the subsequent data analysis and wrote manuscript. H. Y. conceived and designed this  
824 project, provided thought guidance, wrote part of the manuscript and revised manuscript. J. Z. and  
825 D. Z. assisted in data analysis and summary. P. Z., Y. L. and N. M. provided consultant. K. W.  
826 assisted in the experimental results analysis.  
827