Formation of brine channels in sea ice

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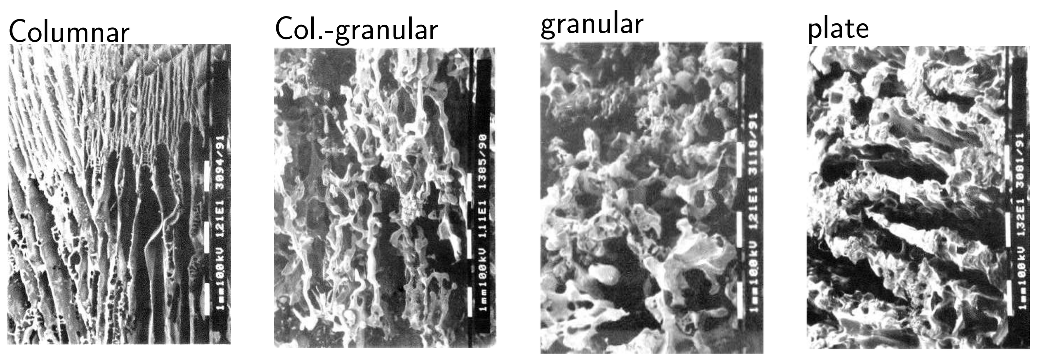
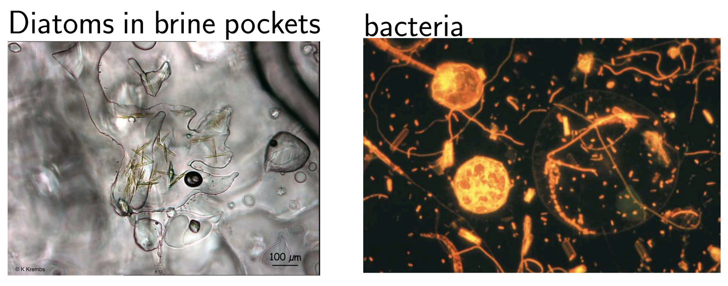
Different ice textures as habitat for micro-organisms

Columnar Col.-granular granular plate



Weissenberger, Ber. Polarforsch. 111 (1992)

Diatoms in brine pockets bacteria Dieckmann



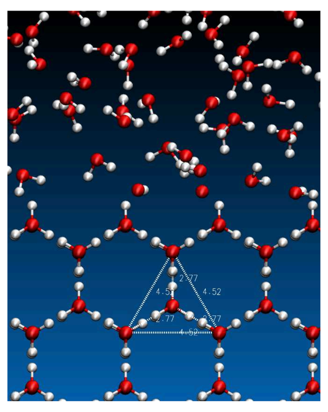
• carbon consumption of organisms in brine channels: 18% in southern ocean

Minimal microscopic model

1. Molecular structure of water and ice by "tetrahedricity"

$$u = \frac{1}{15 < l^2 >}\sum_{i,j}(l_i - l_j)^2$$

l_i lengths of six edges by four nearest neighbors



ice: ideal tetrahedron $M_T = 0$
water: random structure $M_T = 1$

2. Salinity v
free energy density

$$\frac{D_{\rm ice}}{2}(\nabla u)^2 + \frac{a_1}{2}u^2 - \frac{a_2}{3}u^3 + \frac{a_3}{4}u^4 + \frac{h}{2}u^2 v + \frac{D_{\rm salt}}{2}v^2$$

a_1... freezing parameter (phase transition)
a_3... structure parameter (nonlinear)
a_2... first-order phase transition
h... ice-water coupling (reaction rate)
$D_{\rm ice}$, $D_{\rm salt}$ diffusion coefficients of ice and salt

Time evolution of Cahn-Hilliard-type

• conservation of salt mass, demand balance equation $\partial v/\partial t = -\nabla\vec{j}$
• current generalized force $\vec{j} \sim \vec{F}$ by potential $\vec{F} = -\nabla P$
• potential in turn by free energy density $P = \delta f/\delta v$

dimensionless time $\tau = D_{\rm salt}a_2^2 t/h^2$, space $\xi = a_2 x/h$, order parameter $\psi = h^2 u/D_{\rm salt}a_2$, and salinity $\rho = h^3 v/D_{\rm salt}a_2^2$

$$\frac{\partial\psi}{\partial\tau} = -\alpha_1'\psi + \psi^2 - \alpha_3\psi^3 - \psi\rho + D\frac{\partial^2\psi}{\partial\xi^2}, \qquad \frac{\partial\rho}{\partial\tau} = \frac{1}{2}\frac{\partial^2\psi^2}{\partial\xi^2} + \frac{\partial^2\rho}{\partial\xi^2}.$$

time-dependent Ginzburg-Landau equations couple 2 order parameters by 3constants:

1. freezing parameter $\alpha_1' = a_1 h^2/a_2^2 D_{\rm salt}$
2. structure parameter $\alpha_3 = \frac{a_3 D_{\rm salt}}{h^2}$
3. diffusivity $D = \frac{D_{\rm ice}}{D_{\rm salt}}$ with $\alpha_1,' \alpha_3,\ D > 0$

Thermodynamics

uniform stationary free energy density $f(\Psi_0, \rho_0) = \frac{\alpha_1}{2}\psi_0^2 - \frac{1}{3}\psi_0^3 + \frac{\alpha_3}{4}\psi_0^4$

• Freezing-point depression since $\alpha_1(T) = \alpha_1'(T) + \rho_0$ (higher temperature than α_1')

• at $T_c^0 = 233.15K$ vanishes $\alpha_1(T) = \tilde{\alpha}_1(T - T_c^0)$

• freezing point depression $\Delta T = -\frac{\rho_0}{\tilde{\alpha}_1}$
→ latent heat of water-ice phase transition $\Delta H = 6kJ/mol$ and a dissociation ratio of $x = (n_{Na^+} + n_{Cl^-})/n_{H_2O} = 1/50$, Clausius-Clapeyron: $\Delta T = -xRT^2/\Delta H = -2K$
→ specific heat $c = -T_c^0\frac{\partial^2 f(\psi_0^+(T))}{\partial T^2} = \frac{8}{81}\frac{T_c^0}{\alpha_3^3(T_c - T_c^0)^2}$

energy scale difference of latent heat of water freezing $K_E = L(0°C) - L(-40°C) = 98J/g$, our theory: $c_{spec} = K_E c = 2.14J/gK$

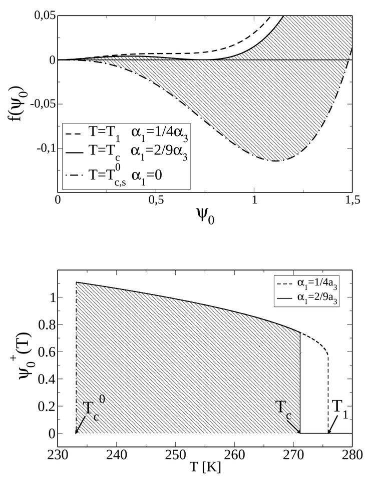
$\rightarrow \alpha_3 = 0.9$

Supercooling/heating only by α_1, α_3

• $\alpha_1 > 1/4\alpha_3$, minimum at 0: disordered state
• $\alpha_1 \le \frac{1}{4\alpha_3} = \alpha_1(T_1)$ second minimum, coexistence curve, borderline represents super-heating
• $\alpha_1(T_c) = \frac{2}{9\alpha_3} < \alpha_1(T) < \frac{1}{4\alpha_3}$ ordered phase metastable, (ice formation possible)
• $\alpha_1 \le \alpha_1(T_c)$ ordered phase stable, jump at T_c latent heat, first-order phase transition
• super-cooling T_c^0, freezing-point T_c, super-heating

$$T_1 = \frac{9}{8}T_c - \frac{1}{8}T_c^0$$

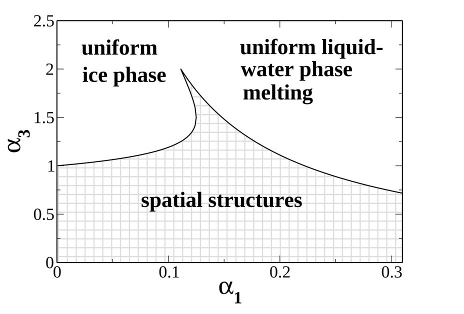
• homogeneous nucleation at super-heating > 5°C, fresh water ($T_c = 273.15$K and $T_c^0 = 233.15$K) we have upper limit of super-heating $T_1 = 4.96$°C in agreement with experiment K. Baumann et al. Z. Phys. B Cond. Matt. 56 (1984) 315



$\rightarrow \alpha_3 = 0.9, \qquad \alpha_1 = 0.2$

Linear stability analysis

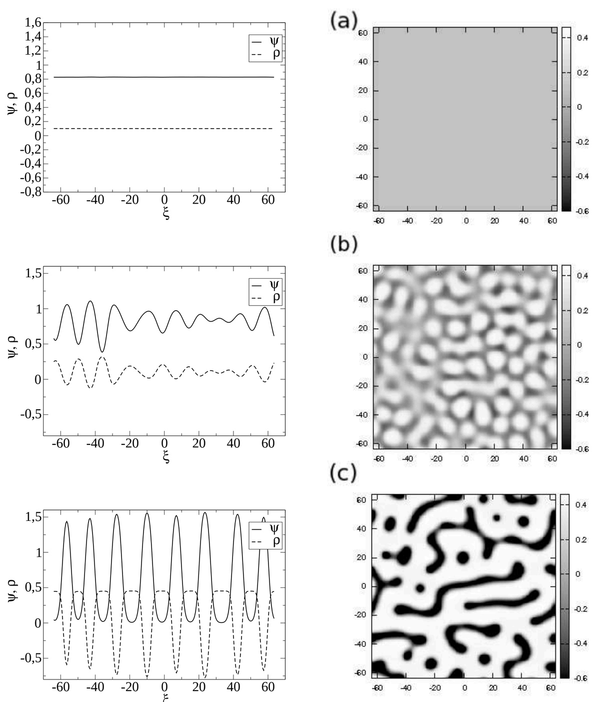
linear stability analysis $\bar{\rho} = \bar{\rho}_0 e^{\lambda(\kappa)\tau + i\kappa\xi}$ around the disordered and ordered phase
$\lambda(\kappa) > 0$ allows fluctuation with wave-vector κ to grow exponentially in time
time-oscillating structures would appear only if ${\rm Im}\lambda(\kappa) \ne 0$, never in our model



phase diagram where spatial structures can occur (checked)

• structure parameters α_1 determines brine channel formation:
• small α_1 means low temperatures or low salinities and consequently freezing process
• uniform ice phase for sufficiently large α_3 and a precipitate of salt
at higher α_1 higher temperatures or higher salinities inducing a melting with uniform liquid water phase and dissolved salt
• spatial structures can only appear in the instability region (maximal point $\alpha_1 = 1/9$ at $\alpha_3 = 2$)

Time evolution



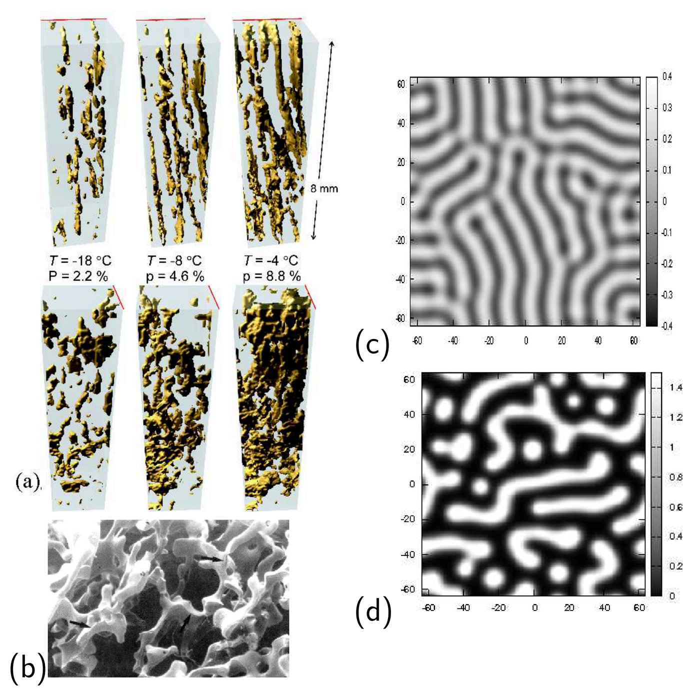
1D (left) and 2D (right) vs. spatial coordinates $\tau = 10, 150, 500$ (from above) with $\alpha_3 = 0.9$, $\alpha_1 = 0.2$,

$$D = \frac{D_{\rm salt}}{D_{ice}} \approx 0.5$$

by $D_{\rm salt}$ at $T_c^0 = -1.9$°C [S. Maus 2007]

and $D_{\rm ice}$ by reorientation rate H_2O [A. Bogdan 1997] and correlation length [D. Eisenberg and W. Kauzmann 2002]

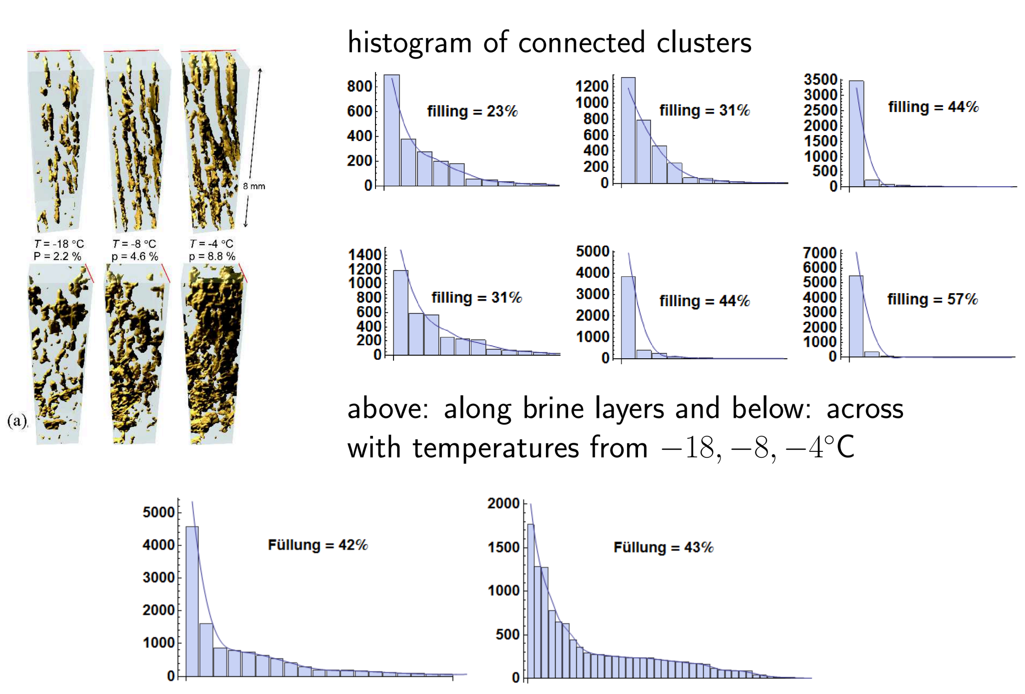
Comparison with experiment: 1. morphology



(a) Imaging brine pore space with X-ray computed tomography D. J. Pringle et al. J. Geophys. Res. Oceans 114 (2009) C12017 upper images: along brine layers, bottom: across
(b) Scanning electron microscopy image of cast of brine channels Weissenberger
(c) long-time Turing
(d) phase field structure with salinity conservation

Comparison with experiment: 2. percolation threshold

histogram of connected clusters



above: along brine layers and below: across with temperatures from $-18, -8, -4$°C

$\alpha_1' = 0.1$, and $D = 0.5$ and $\alpha_3 = 0.9$ (left) compared to $\alpha_3 = 1$ (right)

Comparison with experiment: 3. structure size

• fastest-growing wave-vector $\kappa_c(D, \alpha_1, \alpha_3)$ sets structure by $2\pi/\kappa_c$
• critical domain size as function of freezing point depression $\lambda_c = \frac{2\pi}{k_c} = \frac{2\pi}{\kappa_c}\frac{h}{a_2} = \frac{2\pi}{\kappa_c}\sqrt{\frac{D_{salt}\rho_0}{\tilde{a}_1|\Delta T|}}$

1. Pure sea ice:
• our choice $\alpha_3 = 0.9, \alpha_1 = 0.2$ (super-cooling $\Delta T_{sup} = 6.3$K) and $D = D_{ice}/D_{salt} = 0.5$: dimensionless pattern size of 13.81
• rate of re-orientations of H_2O-molecules determines $\tilde{a}_1 = 1250K^{-1}s^{-1}$
• we obtain critical domain size $\lambda_c = 0.8\mu$m in agreement with sea ice platelet spacing $\lambda_{max} \approx 1\mu$m from morphological stability analysis (Weissenberger, Prible, Golden)

2. Size for natural conditions
• by upper limit of the instability region $\alpha_3 = 1.99$ and freezing parameter $\alpha_1 = 0.111482$, realistic description of seawater at 0.032K super-cooling and a lower limit of the super-cooling region of fresh water at -18.78°C
• we obtain dimensionless structure size $2\pi/\kappa_c = 4975.25$ and critical domain size $\lambda_c = 198\mu$m in agreement with observed values $3 - 1000\mu$m average 200μm

Summary

• model for brine channel formation with two coupled order parameters, tetrahedricity and salinity preserving mass conservation
• linear stability analysis provides phase diagram (two parameters)
• region of instabilities determined exclusively by freezing parameter and specific heat or structure parameter not by diffusivity (Touring model)
• parameters describe thermodynamical properties of water like super-heating, super-cooling, freezing temperature and latent specific heat simultaneously
• time-dependent evolution solved and brine channel texture in agreement with the experimental values
• physical justification of parameters by other properties of water leads to a better description of brine channel texture by mass conservation: internal consistency of the model
• Outlook: New dynamical mechanism of antifreeze proteins (new project)

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