

Influence of AFPs on the crystal growth in solidification of water

Fachhochschule
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Applied Sciences



AWI Alfred-Wegener-Institut
für Polar- und Meeresforschung

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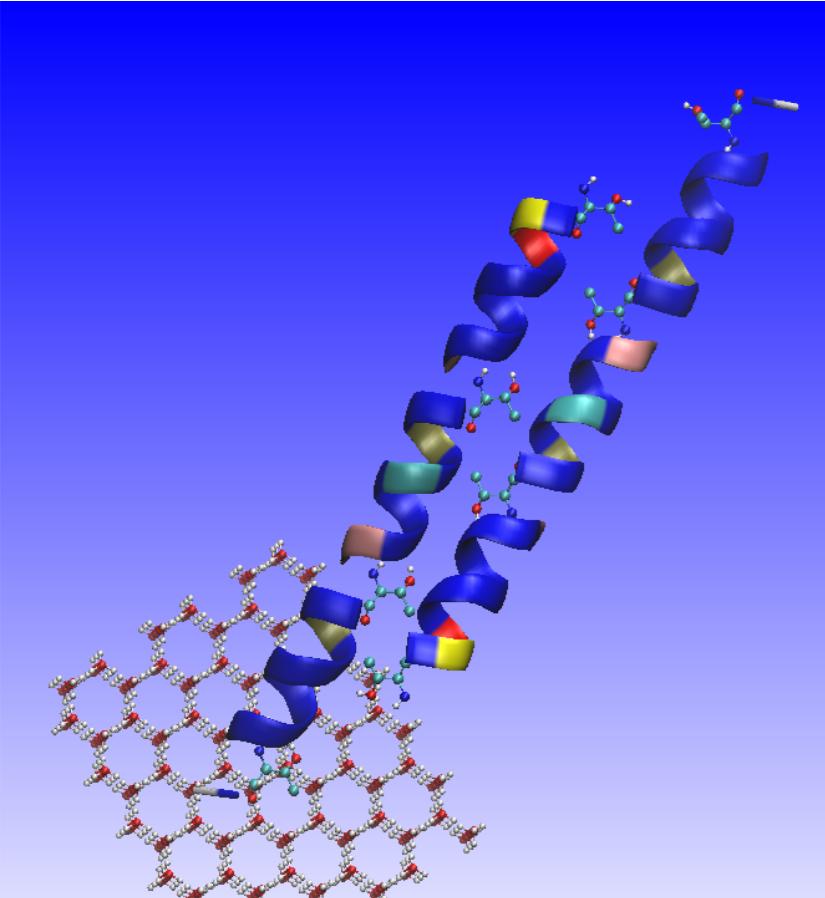
HZDR

HELMHOLTZ
ZENTRUM DRESDEN
ROSSENDORF

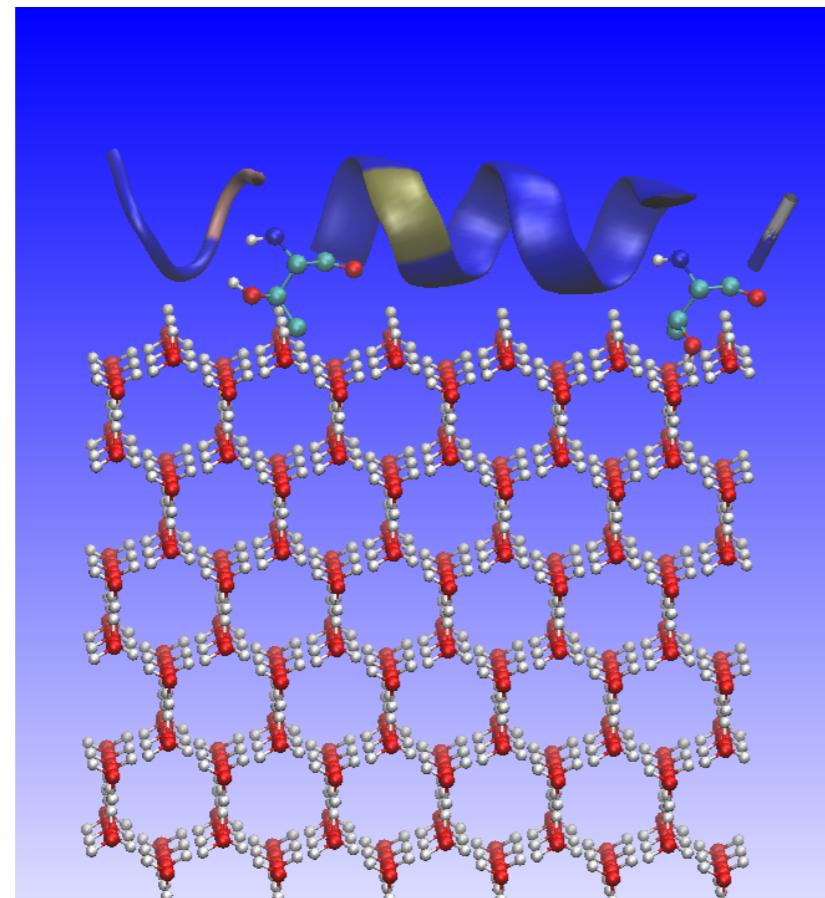
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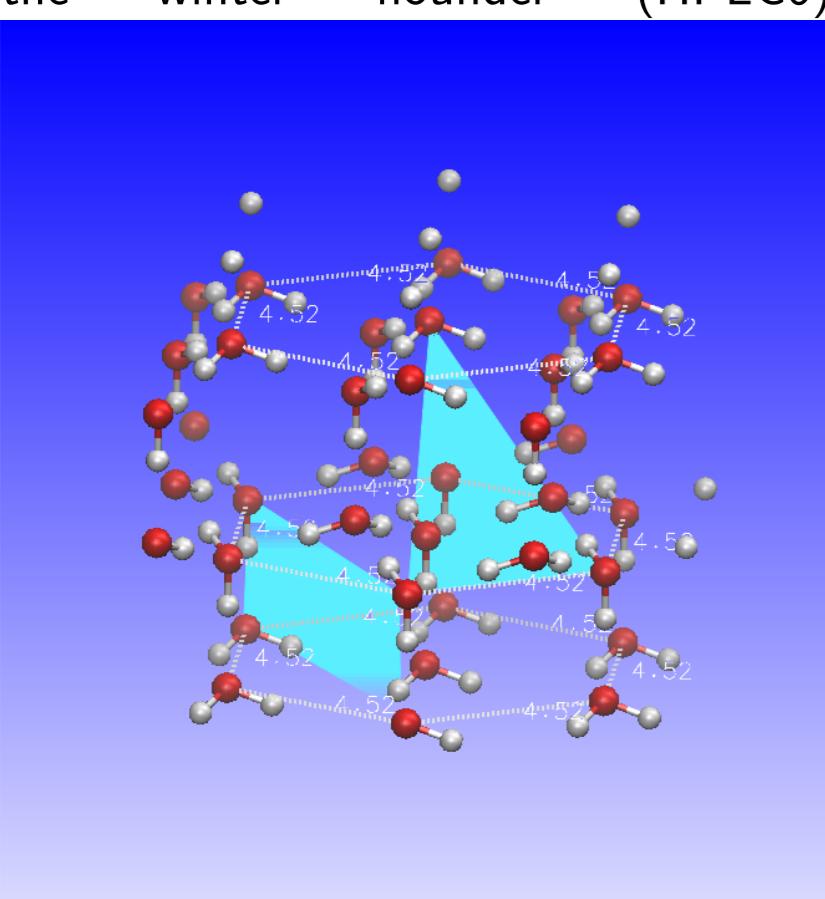
Introduction



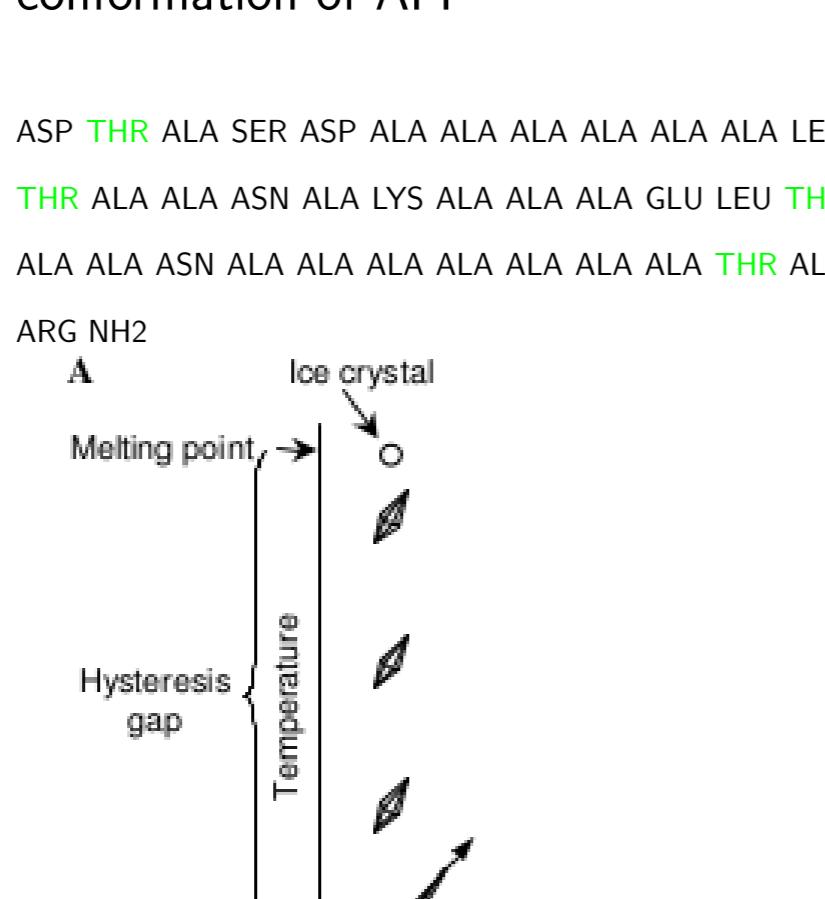
Alanine rich α -helical protein of the winter flounder (HPLC6)



Most energetically stable binding conformation of AFP



possible adsorption planes for AFPs



Kristiansen et al., Cryobiology 51 (type 1)

Dimensionless equations

$$\frac{\partial \psi}{\partial \tau} = \frac{\partial^2}{\partial \xi^2} \left(\left(\frac{1}{6} - a + a^2 \right) \psi + \left(a - \frac{1}{2} \right) \psi^2 + \frac{1}{3} \psi^3 - \alpha_1 \rho - \frac{\partial^2 \psi}{\partial \xi^2} \right) \quad (5)$$

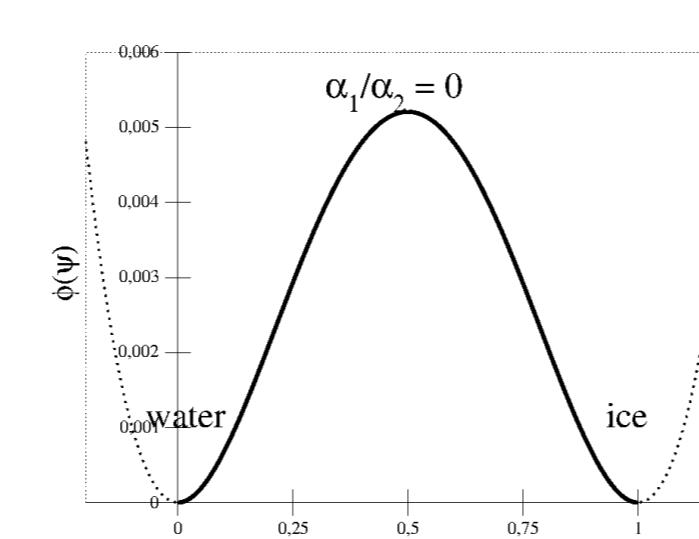
$$\frac{\partial \rho}{\partial \tau} = \frac{\partial^2}{\partial \xi^2} (\psi + \alpha_2 \rho). \quad (6)$$

Free energy density (static case)

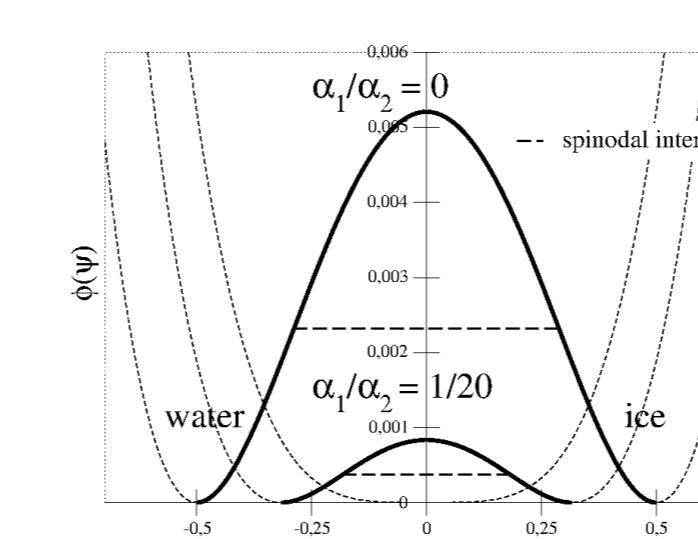
$$\phi(\psi) = \aleph \psi^2 - \frac{1}{6} \psi^3 + \frac{1}{12} \psi^4, \quad a = 0, \quad \aleph = -\frac{\alpha_1}{\alpha_2} + \frac{1}{12} \quad (7)$$

$$\phi(\psi) = -\frac{1}{2} \aleph \psi^2 + \frac{1}{12} \psi^4 + \frac{3}{4} \aleph^2 = \left(\frac{1}{\sqrt{12}} \psi^2 - \frac{\sqrt{3} \aleph}{2} \right)^2, \quad a = \frac{1}{2} \quad (8)$$

Transition into the principal axis: left $a = 0$ (outside), right $a = \frac{1}{2}$ (into the principal axis)



$\alpha_1/\alpha_2 = 0$



$\alpha_1/\alpha_2 = 1/20$

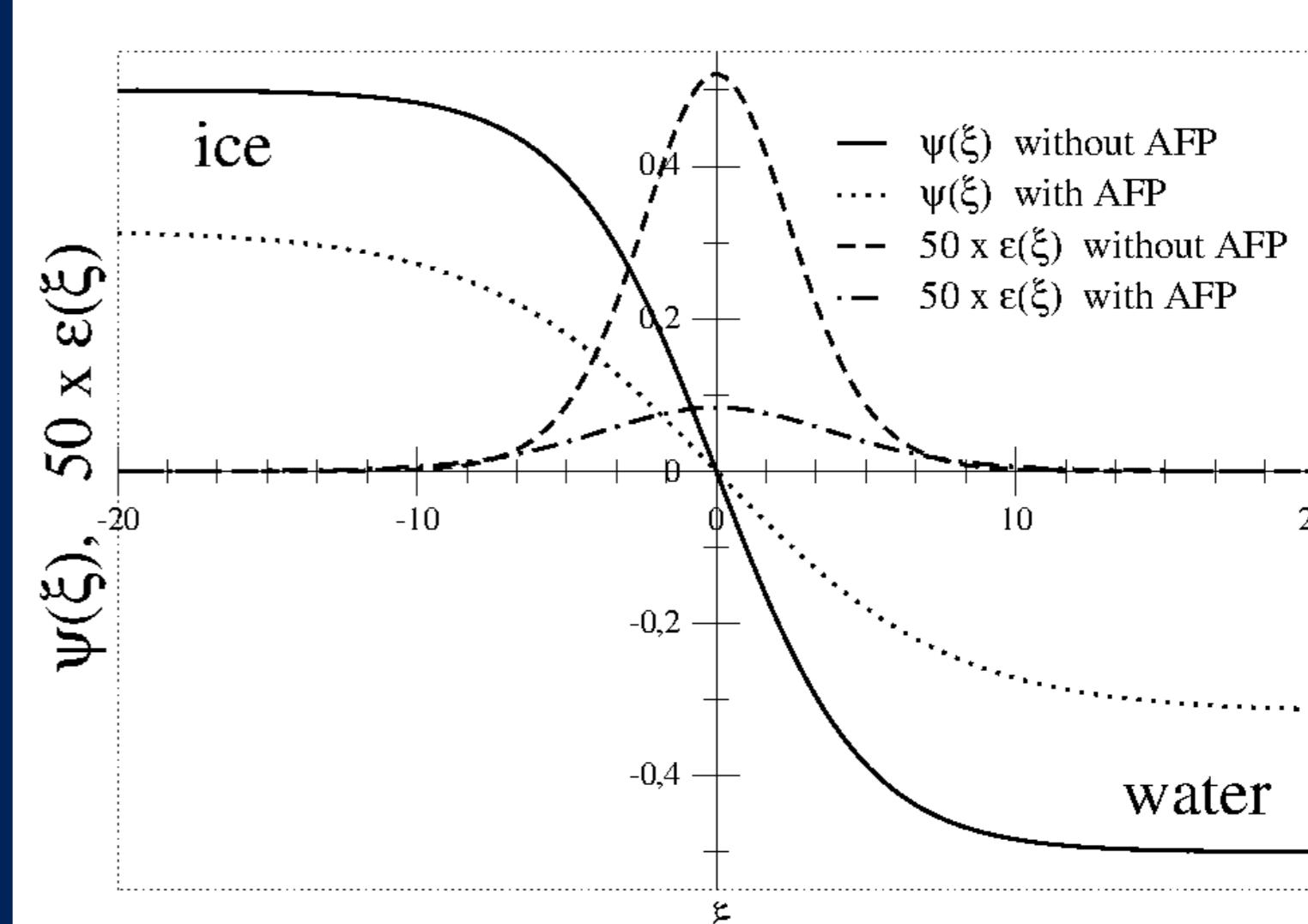
free energy density $\phi(\psi)$ for pure ice/water (upper line, $\alpha_1/\alpha_2 = 0$), for ice/water/AFPs (lower line, $\alpha_1/\alpha_2 = \frac{1}{20}$), for higher AFP concentration (dotted line, $\alpha_1/\alpha_2 = \frac{1}{12}$, limit case, the double well vanishes)

Interfacial energy

Kink solution: $\psi(\xi) = \sqrt{3\aleph} \tanh \left(-\frac{\sqrt{3\aleph}}{\sqrt{6}} (\xi - \xi_1) \right) \quad (10)$

Interfacial energy density

$$\varepsilon = \phi(\psi) + \frac{1}{2} \left(\frac{\partial \psi}{\partial \xi} \right)^2 = 2\phi(\psi) = \left(\frac{\partial \psi}{\partial \xi} \right)^2 = \frac{3}{2} \aleph^2 \operatorname{sech}^4 \left(\frac{\sqrt{\aleph}}{\sqrt{2}} \xi \right) \quad (11)$$



ice

water

— $\psi(\xi)$ without AFP

... $\psi(\xi)$ with AFP

-- $50 \times \varepsilon(\xi)$ without AFP

- - - $50 \times \varepsilon(\xi)$ with AFP

$$\zeta = \lim_{\Lambda \rightarrow \infty} \int_{-\Lambda}^{\Lambda} \varepsilon(\xi) d\xi = \frac{3}{2} \aleph^2 \lim_{\Lambda \rightarrow \infty} \int_{-\Lambda}^{\Lambda} \operatorname{sech}^4 \left(\frac{\sqrt{\aleph}}{\sqrt{2}} \xi \right) d\xi = 2\sqrt{2}\sqrt{\aleph^3} \quad (12)$$

Interfacial energy: $\zeta = 2\sqrt{2} \sqrt{\left(-\frac{\alpha_1}{\alpha_2} + \frac{1}{12} \right)^3} = \begin{cases} 0 & \text{for } \frac{\alpha_1}{\alpha_2} = \frac{1}{12} \\ \frac{1}{6\sqrt{6}} & \text{for } \frac{\alpha_1}{\alpha_2} = 0 \end{cases}$

- high AFP activity decreases interfacial energy and inhibit interface formation

Mechanisms

Colligative phenomena

Freezing point depression

$\Delta T = T_0 - T = \frac{k_B T_0^2}{\Delta H_0} x_b$

proportional to the concentration of the solvent species x_b

Adsorption inhibition

Gibbs-Thomson (Kelvin) model

$\Delta T = T_0 - T = \frac{2\Omega\gamma T_0}{\rho_{min} \Delta H_0}$

proportional to the interfacial energy γ and inversely proportional to the radius of the sphere ρ_{min}

Phase field equations

$$\mathfrak{F} = \int_{x_1}^{x_2} \left(f(u(x), v(x)) + c \left(\frac{\partial u}{\partial x} \right)^2 \right) dx \quad (1)$$

$$f(u, v) = \beta u + \lambda u^2 - 2\lambda u^3 + \lambda u^4 - a_1 u v - \frac{1}{2} a_2 v^2. \quad (2)$$

Cahn-Hilliard-type equations

$$\frac{\partial u}{\partial t} = -\frac{\partial^2}{\partial x^2} \left(-\frac{\delta \mathfrak{F}}{\delta u} \right) = \frac{\partial^2}{\partial x^2} \left(2\lambda u - 6\lambda u^2 + 4\lambda u^3 - a_1 v - 2c \frac{\partial^2 u}{\partial x^2} \right) \quad (3)$$

$$\frac{\partial v}{\partial t} = -\frac{\partial^2}{\partial x^2} \left(\frac{\delta \mathfrak{F}}{\delta v} \right) = \frac{\partial^2}{\partial x^2} (a_1 u + a_2 v) \quad (4)$$

u = structural order parameter for water/ice
 v = field for AFPs
 $\frac{1}{2} a_2 v^2$ = diffusion potential
 β_1 = free energy density scale
 β deviation from equilibrium = desalination rate
 c = coefficient of the nonlocal square gradient term

Summary

- Dynamical mechanism found which inhibits the growth of ice crystals
- Decisive role of interface energy, AFPs enlarge the interface region
- Description with the help of coupled nonlinear phase field equations where the order parameter is coupled to the concentration of AFPs

Phase field equations

$$\mathfrak{F} = \int_{x_1}^{x_2} \left(f(u(x), v(x)) + c \left(\frac{\partial u}{\partial x} \right)^2 \right) dx \quad (1)$$

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Cahn-Hilliard-type equations

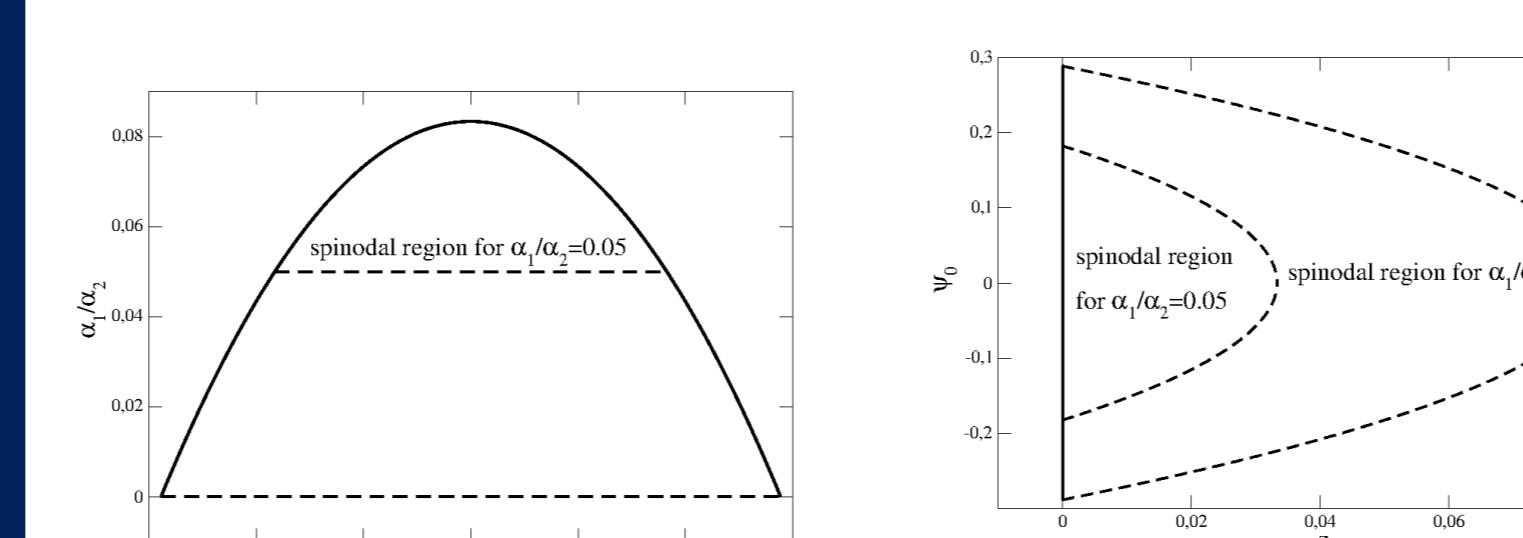
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Spinodal representations

$$\frac{\alpha_1}{\alpha_2} = \frac{1}{12} - \psi_0^2 \quad -\sqrt{\frac{1}{12} - \frac{\alpha_1}{\alpha_2} - z} < \psi_0 < \sqrt{\frac{1}{12} - \frac{\alpha_1}{\alpha_2} - z}$$

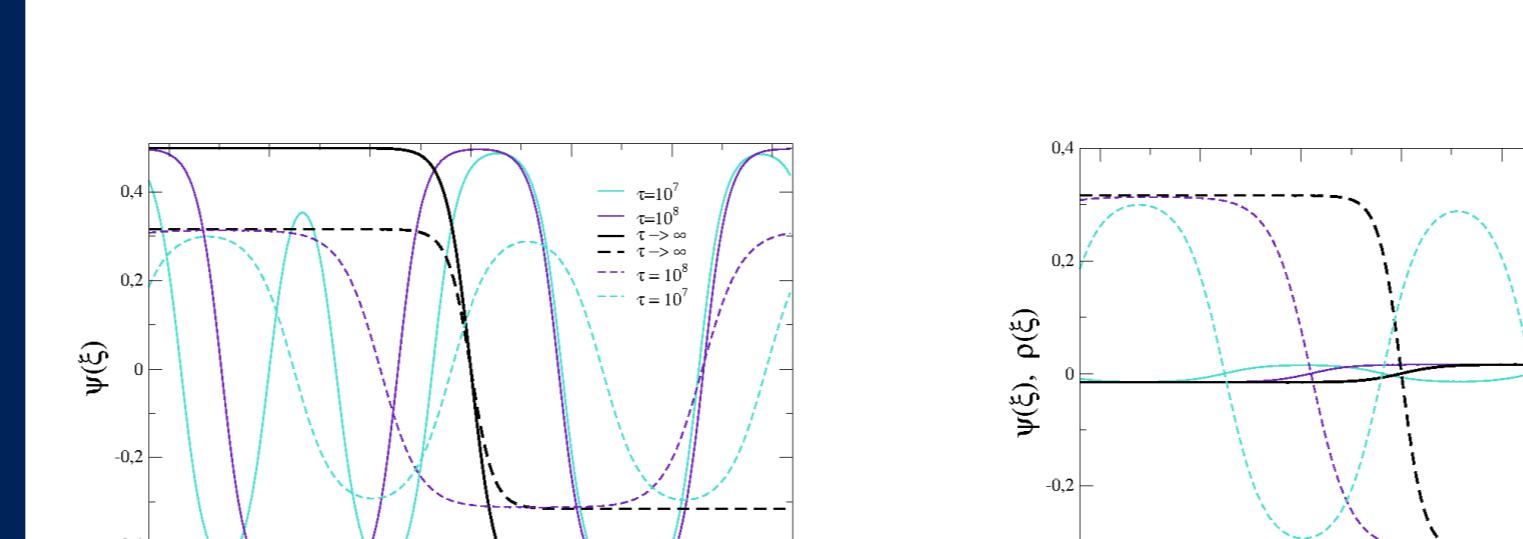


spinodal region for $\alpha_1/\alpha_2 = 0.05$

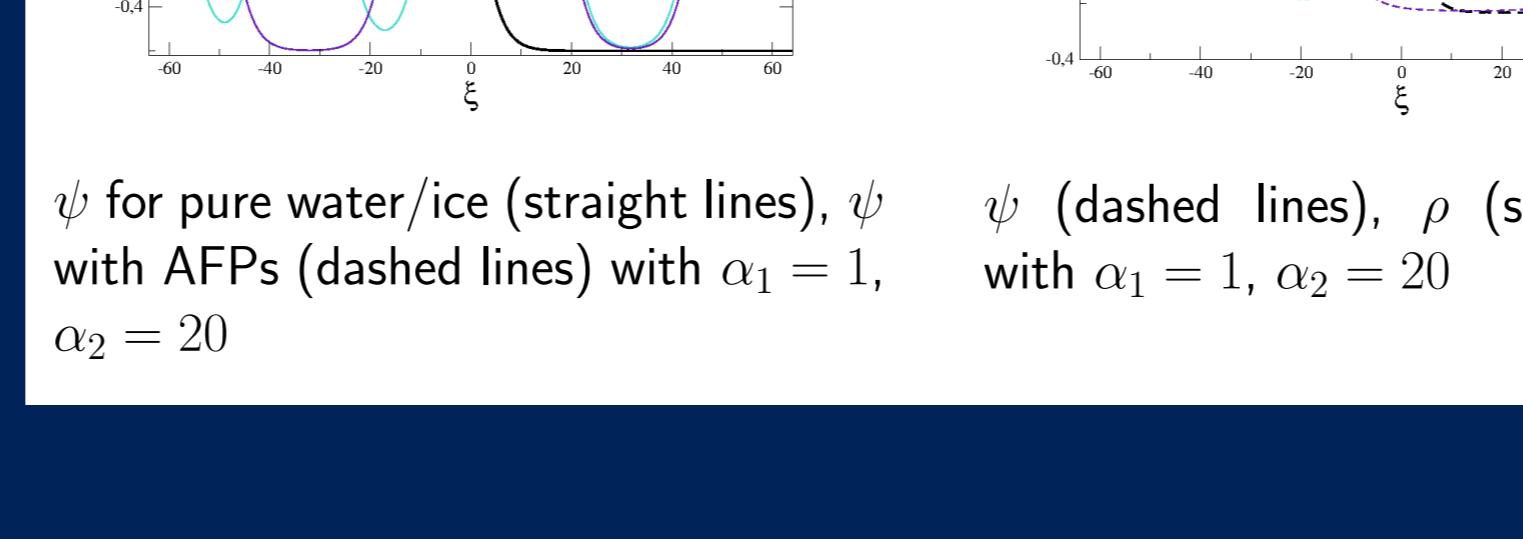
spinodal region for $\alpha_1/\alpha_2 = 0.05$

spinodal region for $\alpha_1/\alpha_2 = 0.05$

Time Evolution



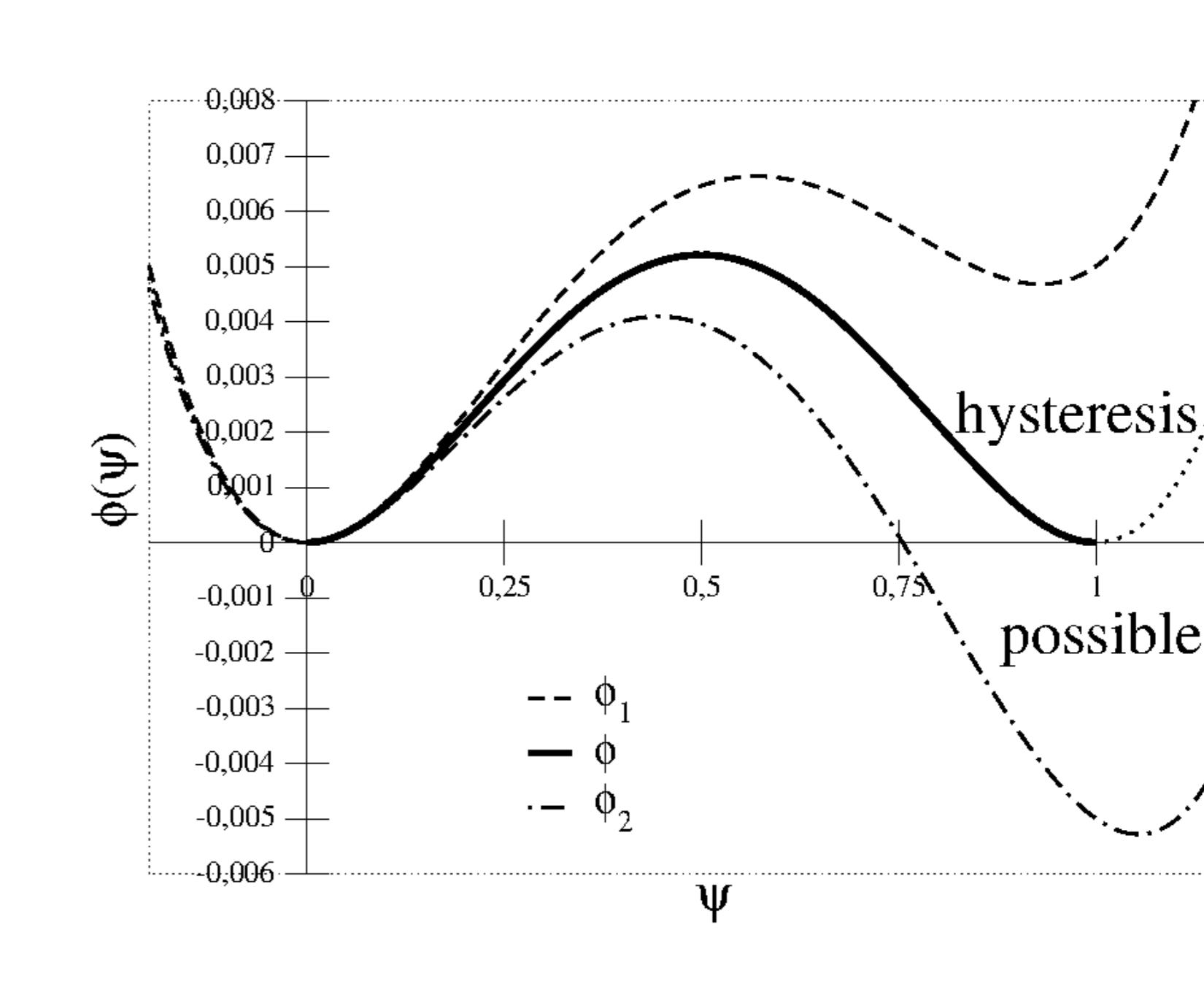
ψ for pure water/ice (straight lines), ψ with AFPs (dashed lines) with $\alpha_1 = 1$, $\alpha_2 = 20$



ψ (dashed lines), ρ (straight lines) with $\alpha_1 = 1$, $\alpha_2 = 20$

Hysteresis

$$\phi_{1,2} = \left(\frac{1}{12} \pm 0.005 \right) \psi^2 - \frac{1}{6} \psi^3 + \frac{1}{12} \psi^4$$



hysteresis

possible

-- ϕ_1

— ϕ

- - - ϕ_2

Further activities

- Computation of the thermal hysteresis

Funding via the Deutsche Forschungsgemeinschaft (SPP 1158), DFG-CNPq project 444BRA-113/57/0-1, the DAAD and financial support by the Brazilian Ministry of Science and Technology is acknowledged.

DFG-SCHWERPUNKTPROGRAMM 1158
ANTARKTIS FORSCHUNG
mit vergleichenden Untersuchungen in arktischen Eisgebieten