Dependence of the form of crystallization front on boundary conditions in a method of the horizontal unidirectional solidification

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Abstract. The processes of water and heptadecane crystallization are investigated numerically and experimentally by a method of the horizontal unidirectional solidification. Water is the simulator of melts with inverse dependence of density on temperature. Influence of boundary conditions on the upper surface of melt layers in regimes of non-stationary buoyancy-thermocapillary induced convection on spatial form s of a flow, temperature fields and solid-melt interface shape is investigated. Cases with rigid top boundary and with free boundary of melt layer are studied taking into account the thermocapillary effect.

1. Introduction
The method of horizontal unidirectional crystallization (HUC) is one of the main methods for obtaining single crystals from melts [1-3]. In the HUC method, crystal growth occurs under conditions of conjugate convective heat transfer in the regime of nonstationary thermogravitational or buoyancy-thermocapillary induced convection, depending on the conditions at the upper boundary. A simplified model of the technological process of HUC is the process of crystallization of the melt in a rectangular cavity with vertical walls heated to different temperatures [3-5]. The shape of crystallization fronts and the temperature field and the temperature gradients in the solidified material depend on the features of local heat transfer, on which the crystallographic characteristics of the crystals depend uniformly [2-4, 6]. The use of water as a melt imitation fluid in the physical and numerical modeling of convective heat transfer in HUC is due to the inverse dependence of its density on temperature in the vicinity of 4°C. For example, the melts of gallium and eutectic cadmium-mercury-tellurium and some other substances and materials (bismuth, stibium) have similar dependences. The inverse dependence of the melt density on temperature near the crystallization temperature introduces features into the hydrodynamics of the melts at the crystallization front and in the distributions of local heat fluxes. Fundamental studies of the kinetics of crystallization in the water-ice system were considered in the early works from the crystallographic point of view [7]. Nonstationary heat transfer in the natural convection of water was studied mainly for the purpose of studying the processes of formation, growth and melting of ice under natural conditions.

This work is a logical continuation of convection studies in rectangular cavities in single-phase media and in the presence of crystallization [4-6]. The results obtained in [4, 5] under boundary conditions of the first kind do not allow one to estimate the effect of conjugate convective heat transfer
on nonstationary temperature fields and temperature gradients in a crystal. In this paper, numerical simulation of the nonstationary conjugate convective heat transfer and its effect on the shape of the water crystallization front is performed taking into account the inverse dependence of the melt density on temperature. The results of numerical simulation are compared with the data of the physical experiment with the crystallization of water and heptadecane and supplement the experiment on the distribution of temperature in the liquid and in the solid at different stages of crystal growth.

2. Statement of the problem

Two problems with different boundary conditions at the upper boundary were solved, in a nonstationary two-dimensional conjugate formulation in Cartesian coordinates with allowance for the heat of crystallization. The geometry of the computational domain is chosen to be the same: the length of the water layers is 200 mm, height is 12.5 mm. At the initial instant of time, the design area consists of a melt layer that, after a sudden cooling of the right vertical wall below the crystallization temperature, begins crystallizing. The initial temperature of the system is maintained on the left vertical wall. Convective heat transfer in a fluid is described by the dimensionless system of Navier-Stokes equations and energy in the Boussinesq approximation, written in terms of temperature, vorticity and stream function:

\[
\frac{\rho_f(T)}{\rho_f} \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) - \frac{1}{Pr} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right),
\]

\[
\frac{\rho_f(T)}{\rho_f} \left( \frac{\partial \omega}{\partial t} + u \frac{\partial \omega}{\partial x} + v \frac{\partial \omega}{\partial y} \right) = \left( \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) + Gr \frac{\partial T}{\partial x},
\]

\[
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\omega, \quad v = -\frac{\partial \psi}{\partial x}, \quad u = \frac{\partial \psi}{\partial y}, \quad Gr = \frac{g \cdot \beta_f(T) \cdot H^3 \Delta T}{\nu_f^2}.
\]

The equation of energy in the crystallization zone is modified taking into account the heat of crystallization and looks as follows [8]:

\[
\left( 1 + \frac{R}{c_p(T_f - T_s)} \right) \left( \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = \frac{\lambda_s}{\lambda_f \cdot Pr} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right)
\]

Conductive heat transfer in a crystal is described by the equation of thermal conductivity:

\[
\frac{\rho_f c_{pf}}{\rho_f c_{pf}} \frac{\partial T}{\partial t} + \frac{\lambda_s}{\lambda_f \cdot Pr} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) = 0,
\]

if the final thermal conductivity of the bottom wall of the cavity is taken into account, the conductive heat exchange is described by the equation of thermal conductivity:

\[
\frac{\rho_f c_{pf}}{\rho_f c_{pf}} \frac{\partial T}{\partial t} + \frac{\lambda_s}{\lambda_f \cdot Pr} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) = 0.
\]

When solving the equations of motion, the temperature dependence of the coefficient of volumetric thermal expansion of water \( \beta_f(T) \) and its density \( \rho_f(T) \) is taken into account. To calculate the constant parameters, fixed values of the thermal properties of water and ice at 0°C were used. Water properties: density \( \rho_f = 999.839 \text{ kg/m}^3 \); coefficient of kinematic viscosity \( \nu_f = 1.793 \times 10^{-6} \text{ m}^2/\text{s} \); coefficient of thermal conductivity \( \lambda_f = 0.554 \text{ W/m*K} \); Specific heat \( c_{pf} = 4218 \text{ J/kg*K} \); The heat of crystallization \( R = 333.7 \text{ kJ/kg} \) [10]. Properties of ice: \( \rho_s = 916.2 \text{ kg/m}^3 \); \( \lambda_s = 2.2 \text{ W/m*K} \); \( c_s = 2050 \text{ J/kg*K} \). \( T_f \) is the
temperature of the liquid before the crystallization front at a distance corresponding to the distancing of the interface advance in one time step. $T_0$ is crystallization temperature. At solid boundaries in the system, including the liquid-crystal interface, the conditions for adhesion and non-flow are specified:

$$ \psi |_{t} = 0, \omega |_{t} = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}, $$

if the upper surface is free from friction and deformation, then on it: $\omega |_{t} = 0$. If the thermocapillary effect is taken into account, then:

$$ Ma = \left( \frac{\partial \sigma}{\partial T} \right)_{\alpha, \mu} \frac{H}{\alpha, \mu} \Delta T, \omega |_{t} = \frac{Ma dT}{Pr} \frac{\partial}{\partial x}. $$

The boundary condition for the vortex is obtained from the field of the stream function, using the conjugate resultant method [9]. The horizontal boundaries are considered adiabatic. If the final thermal conductivity of the bottom wall of the cavity is taken into account, the thermal insulation condition is placed on its external horizontal surface. At the liquid-crystal interface, the ideal thermal contact is specified, i.e. condition of continuity of temperature and heat flow. The problem was solved in a dimensionless form, the height of the liquid layer $H$ was chosen as the scale of the geometric dimensions. The scales $\nu_f/H$ and $H^2/\nu_f$, respectively, were used for velocity and time. The temperature scale is $\Delta T = T_1 - T_2$, where $T_1$ and $T_2$ are the temperatures on the hot and cold walls, respectively.

The calculations were carried out by the finite element method using an adaptive triangular grid with the number of nodes from 35,000 to 65,000. The triangular grid tracks the position of the crystallization front at each time step and thickens on both sides of it, and also to varying degrees to all boundaries of the computational domain. The program implements an iterative process, which, if necessary, substitutes the necessary values of the variables from the previous steps and the calculated values of the coefficients from the parameters. At the same time, the temperature is first, then the vortex, the stream function. In the iteration process, the relaxation method was used at a time step. The finite-element SLAU is solved by means of the local-optimal scheme (LOS) with LU preconditioning.

### 3. Analysis of results

With a suddenly applied drop in temperature between the hot and cold walls at temperatures of ±10°C, a convective flow develops from the isothermal state of the system at a temperature $T = +10^\circ C$. At the initial instant of time, when the right wall is suddenly cooled to -10°C, the temperature of water, which is much higher than +4°C in the main volume, in exact correspondence between the water density and the temperature in the nearest vicinity of the cold wall, begins dropping. In the lower part of the cavity a stream of water leaving the cold wall is formed. Thus, the situation is similar to the behavior of a liquid with a normal temperature dependence of the density near the suddenly cooled wall. Figures 1 and 2 show the evolution of fields of the isotherms and stream function isolines at a rigid upper boundary (figure 1) and at a free surface with allowance for the thermocapillary effect (figure 2). For both cases at the initial moments of time, superheated water with excessive buoyancy accumulates in the upper part of the layer, and here the growth rate of the ice crust is reduced because of the hot liquid inleakage. In the case of a rigid upper boundary, the situation of monotonic growth in the thickness of an ice layer with a smooth surface is maintained until the critical volume of water is cooled. The amount of supercooled water steadily increases with time in the near-bottom region at the crystallization front. When a critical mass of liquid with a temperature from 0°C to +4°C accumulates, a vortex with reverse circulation of the liquid forms in the bottom part. An upward flow occurs along the crystallization front. This is seen in figure 1b. Located in the near-bottom area, a convective cell with a temperature below +4°C causes an intensive formation of an ice crust in this region. With an increase in the mass fraction of water with a temperature below the density inversion temperature, this convective cell occupies the entire region from the lower to the upper wall near the crystallization
Figure 1. Fields of isotherms and stream function isolines in the regime of thermogravitational convection with a rigid upper boundary at time instants: a - t (min.) = 6.45; b - 18.07; c - 32.6; d - 102.31.

Figure 2. Fields of isotherms and stream function isolines in the regime of buoyancy-thermocapillary induced convection at time instants: a - t (min.) = 6.45; b - 18.07; c - 32.6; d - 78.12.
The circulation of the liquid, caused by the emergence of a supercooled liquid and its accumulation at the upper boundary, causes an accelerated growth of the crystal in this region, and at one point the crystallization front assumes an almost vertical position (figure 1c). Until the moment of the establishment of the current, this vortex with circulation along the contour in a counter-clockwise direction increases (figure 1d).

The increase in the rate of leakage of heated water onto the resulting ice cake, caused by the thermocapillary effect at the free upper boundary, does not allow the formation of a critical mass of water with a temperature below +4°C. In the regime of buoyancy-thermocapillary induced convection (figure 2), the growth of the ice layer on the vertical wall occurs monotonically until the time $t \approx 13$ min (figure 2a). In the future, the flow loses stability and a system of drifting vortices appears on the boundary of the opposing streams (figure 2b, c). The velocity of fluid flow in a layer with a free upper boundary (figure 3) is substantially higher than in the case of a rigid boundary (figure 4). This is one of the reasons for the instability. The uneven velocity distribution along the free boundary is caused by a nonuniform temperature distribution. The appearance of secondary vortices leads to local temperature perturbations on the free surface and a local manifestation of the thermocapillary effect. This increases the speed of circulation. The temperature field becomes nonstationary and a stream of heated liquid with a pulsating temperature flows onto the crystallization front. The position of the local velocity maxima coincides with the position of the temperature gradient maxima. Periodic crystallization and melting are observed in the upper part of the front. The monotonous growth of the crystal continues in the lower part of the front. Under the steady-state conditions, the flow and the crystal growth process remain pulsating (figure 2d and figure 3b). After the time $t \approx 16$ min, there is noticeable melting of the formed ice (figure 5a) and monotonous growth turns into a pulsating regime (figure 5b). For a regime with a rigid upper boundary, monotonous growth of the ice layer is characteristic over the entire time interval (figure 6).

Experimental and numerical simulation of nonstationary conjugate convective heat transfer and its effect on the shape of the heptadecane crystallization front is performed. Studies were carried out with layers of heptadecane with a free upper boundary. Numerically, in the regime of thermal gravitational-thermocapillary convection, the process of crystallization of heptadecane was studied at values of the dimensional parameters close to the experimental ones. The problem was solved in a nonstationary two-dimensional conjugate formulation by the finite element method, using triangular adaptive grids.

**Figure 3.** The profiles of the vertical velocity component in the central section along the vertical in the regime of buoyancy-thermocapillary induced convection at the instants of time: 1 - $t$ (min.) = 6.45; 2 - 18.07; 3 - 32.6; 4 - 78.12.

**Figure 4.** The profiles of the vertical velocity component in the central section along the vertical in the regime of thermogravitational convection at time points: 1 - $t$ (min.) = 6.45; 2 - 18.07; 3 - 32.6; 4 - 102.31.
Figure 5. Dependence of the crystal mass (ice density) 1 cm thick on time in the regime of buoyancy-thermocapillary induced convection in the present size (a) and on an enlarged scale (b).

Figure 6. Dependence of the crystal mass (ice density) 1 cm thick on the current time in the regime of thermogravitational convection with a rigid upper boundary.

that track the phase boundary, taking into account the heat of the phase transition. Crystallization temperature of heptadecane was \( T_{CR} = 22^\circ C \). This value was taken as a defined zero when going to a dimensionless temperature. The cold wall temperature \( T_1 = 14^\circ C \) (dimensionless \(-0.8\)) and the hot wall temperature \( T_2 = 24^\circ C \) (dimensionless \(+0.2\)) were set at the initial time. The height of the liquid layer was \( H = 10 \) mm; the length of the liquid layer was \( L = 100 \) mm. The bottom of the rectangular cavity was a plexiglas plate with a thickness \( h = 2 \) mm, the lower boundary of the bottom was adiabatic. The upper limit of the fluid was free, without heat transfer, the thermocapillary effect was taken into account. The physical properties of heptadecane were taken at \( T = 22^\circ C \). In the initial state of the system, the Grashof number was \( Gr = g \beta \Delta T \times H^3/\nu^2 = 4038 \), the Marangoni number was \( Ma = (-d \sigma / dT) \times \Delta T \times H/\mu = 1869 \). The time scale was \( \tau = H^2/\nu \). The results of calculations of hydrodynamics and its influence on the evolution of the shape of the crystallization front in time correspond to those observed in the physical experiment. The results of numerical simulation substantially supplement the experiment in the part of the temperature distributions in the liquid and in the solid at different stages of crystal growth. Figures 7 and 8 show the progress of the crystallization front of heptadecane in a "boat" model with a monotonously cooled right vertical wall. During cooling and crystallization by thermocouples, the temperature of the cooled wall and the discrete temperature on the free surface of the liquid were monitored. At the same time, a non-stationary temperature field was measured at the surface of the liquid layer and on the surface of the solidified substance after the crystallization beginning. Processing of thermal imaging films makes it possible to obtain isotherm fields at different times and temperature
Figure 8. The form of the crystallization front of heptadecane at different times: 1 - 4.4 minutes after the onset of crystallization; 2 - 9.6 minutes; 3 - 23.9 min; 4 - 51.4 min; 5 - 98.4 min; 6 - a copper wall; 7 - bottom of the cuvette; 8 - liquid level without a meniscus.

Figure 9. Isotherms on the free surface and walls of the cavetti (region in the crystallization zone). A thick line is the boundary between phases. The time is 29.1 minutes from the beginning of crystallization.

distributions along the surface (figure 9). A video was taken to promote the crystallization front. Computer processing of the digital video film made it possible to determine the shapes of the crystallization front at various times (figure 8). The effect of convective heat transfer is manifested in different rates of crystallization along the height of the melt layer. On the upper part of the FC, a melt is heated on the left wall flows, which, being cooled, falls into the bottom part. The temperature gradients and local heat fluxes in the lower zone of the FC are lower, so the speed of advance of the FC is higher (figures 7, 8). Figure 7 also shows the field of isotherms in the bottom wall of the cavity. The coefficient of thermal conductivity of Plexiglas (0.195 W/m × K) is slightly higher than that of
heptadecane (0.145 W/m × K). It is seen in figure 7 that cooling from below influences the shape of the front in its lower bottom part.

4. Conclusion
Conjugated convective heat exchange was studied in a rectangular cavity filled with water under various boundary conditions at the upper boundary after a sudden cooling of the right vertical wall to a temperature below the crystallization temperature. The conditions at the upper boundary significantly affect the intensity of the convective flow, the shapes of the crystallization fronts, and the growth rate of the mass of the solidified substance. Dependences of the form of the crystallization front on time and the rate of increase in the mass of the solidified substance are obtained. At crystallization of heptadecane, as in the case of water crystallization, the shape of the front and the rate of advance of the front at different levels along the height of the melt layer depend strongly on the intensity of the melt flow. Stratification of the liquid also affects the height of the melt layer. The effect of the thermocapillary effect is less pronounced than in the case of water, despite large temperature gradients along the free surface of the liquid directly in the crystallization front. A significant difference in the spatial forms of flow and temperature distributions is the absence of singularity in the dependence of the density of the liquid on temperature. The obtained numerical results coincide qualitatively with the data of the physical experiment conducted in parallel with numerical simulation. The obtained data can be useful in analyzing crystal growth processes by the method of horizontally directed crystallization of substances with an inverse density dependence on temperature.

Acknowledgement
This research has been executed within the limits of the project III.18.2.5. Number of the state registration is AAAA-A17-117022850021-3.

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