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Heat and mass transfer in porous media with ice inclusions near the freezing-point

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Abstract

Heat and mass transfer in biporous medium of regular structure near the phase transition point is studied theoretically. Large pores contain ice. Small pores are filled with pure water. The thermal and filtration problems for a separate cell of the medium are solved by the anisotropic conductivity method. Heat and mass flows depend linearly on the gradients of the temperature and the water pressure. The Onsager reciprocal relations are confirmed for systems with phase transformations. With the advent of the solid phase (ice) in porous media, the straight transport coefficients multiply several times, and the cross coefficients increase more than one order of magnitude. 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

The freezing-point of water in a confined space is lower than the phase transition point for a bulk system. That value falls with decreasing the cavity size. Distribution of pore size in porous media enables water to be liquid in a range of negative temperature [\[1\]](#page-9-0). This phenomenon plays an important role in the cold region of the Earth because the properties of frozen soils depend essentially on their ice content. Heat transport processes in freezing soil generate mass transfer, redistribution of water content, deformation of soil framework, formation of cryogenic textures, and frost heave. Those changes in the soil are described by various mathemati-

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cal models, the basic elements of which are the laws of heat, water and ice transfer. Most researchers postulate as follows: Fourier's law, Darcy's law and ice immobility relative to soil particles. A few models presume ice mobility. For example, in the model by O'Neill and Miller [\[2\]](#page-9-0) the ice is assumed to be rigid and to move through the mineral framework without resistance owing to regelation.

Numerous investigations have established the considerable role of the temperature factor on mass transfer in freezing soil [\[3\]](#page-9-0). A specific mathematical form of the mass transfer law is defined by the structure of porous media, and, in general, water and ice flows depend on three gradients of temperature, water and ice pressures [\[4\].](#page-9-0) Nearly all theories disregard the effect of mass movement on heat transfer.

This paper purposes to study a problem of stationary heat and mass transfer in the model porous medium, the free space of which is filled by water and ice.

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Nomenclature

2. The definition of the problem and the solution method

A biporous medium with the simplest structure is taken as the subject of the inquiry. All large pores (cavities E_1 in Fig. 1) are equal spheres and their diameter is significantly greater than the size of small pores in region E_2 . The mineral framework of the medium is a rigid body and stabilizes the spatial configuration. The centres of the cavities are located at the rectangular lattice points. The large pores contain ice that may move relative to the framework because of regelation phenomena [\[5,6\].](#page-9-0) On the front side the ice melts, water migrates through the porous medium to the rear side, where it freezes and reshapes the ice inclusion. Melting of the ice is accompanied by the absorption of heat. And freezing gives rise to the inverse process of heat release. An object with the separated inflow and outflow heat sources, total production of which equals zero, is called the heat dipole.

A liquid fills the porous space of element E_2 and may migrate through the porous medium. Assume that all solid phases are rigid and that the liquid is an incompressible fluid.

The basic properties of the model medium are demonstrated by the example of the one-dimensional sta-

re $[K]$ V_i velocity of ice $[m s^{-1}]$ $v_{\rm w}$ velocity of water $\text{[m s}^{-1}\text{]}$ amical force α dimensionless parameter of the cell, $\pi R^2/S_a$ less parameter of the cell, $2R/b$ of fusion λ thermal conductivity $[\text{W m}^{-1}\text{K}^{-1}]$ λ_1 thermal conductivity of ice [Wm⁻¹K⁻¹] onductivity of fine-pored medium K^{-1}] ρ_i ice density [kgm⁻³] $\rho_{\rm w}$ water density [kgm⁻³] inclusion

dient operator

gradient operator, Eq. [\(22\)](#page-5-0)

tionary process of heat transfer with constant temperatures at horizontal boundaries of the sample (Fig. 1).

Fig. 1. Model biporous medium. E_1 —ice, E_2 —fine-pore medium, f—fluid tube at zero horizontal conductivity.

On the one hand, the heat flow does not pass through the lateral faces of the cells (sections B_1, B_2, \ldots) because of space symmetry. On the other hand, the heat flow lines are perpendicular to the horizontal faces of the adjacent cells (sections A_1, A_2, A_3, \ldots) and therefore the tangential component of heat flux vanishes. The last indicates that the temperature is constant at every horizontal section passing through half of the distance between neighbouring elements E1. An elementary cell (C_1, C_2, \ldots) is selected in the ordinary way and represents a fragment of the framework as a rectangular prism with the cavity in centre [\(Fig. 1\)](#page-1-0).

The properties of the model medium noted above allow simplifying a problem of heat and mass transfer in the porous medium as whole and reducing it to studying the transfer processes in the separate cell (Fig. 2). The problem is formulated in the following way: to find the thermal and liquid flow at the bases of the cell as a function of the specified thermodynamic parameters (temperature and pressure) at the horizontal boundaries.

In this paper a treatment of nonequilibrium systems is limited to a range of parameters near the phase transition point. Convection heat transport in the regions of E_1 and $E₂$ is negligibly small in comparison with the conductive transfer. Fix the spherical and orthogonal co-ordinates to the mineral frame and place the Z-axis in parallel with the imposed temperature and pressure gradients.

The heat sources concentrate at the surface of inclusion and therefore an equation for defining the temperature t in two homogeneous regions (E_1 and E_2) of the cell is Laplace's equation:

$$
\Delta t = 0 \tag{1}
$$

with the boundary conditions being the following: at the bases of the cell $t(x, y, -b/2) = t_1$, $t(x, y, b/2) = t_2$; through lateral faces the heat flux is equal to zero. At

Fig. 2. A cell of biporous medium with ice inclusions. S_a —base area. Q_{lat} —latent heat at phase transition.

the ice surface the value of the temperature is continuous: $t|_{r=R-0} = t|_{r=R+0}$ and the temperature gradients are connected by heat balance:

$$
-\lambda_1 F \frac{\partial t}{\partial r}\bigg|_{r=R-0} - \left(-\lambda_2 \frac{\partial t}{\partial r}\bigg|_{r=R+0}\right) = \kappa \rho_1 V_1 \cos \theta
$$

where (r, θ) are spherical co-ordinates. By symmetry, the ice velocity is parallel to the Z-axis, which is reflected in the last relationship.

Liquid flows only in the fine-pore medium E_2 . For that region an equation of filtration is Laplace's equation for pressure p :

$$
\Delta p = 0 \tag{2}
$$

with boundary conditions being the following: $p(x, y, -b/2) = p_1$; $p(x, y, b/2) = p_2$ and the liquid flux is zero through the lateral faces of the cell. The mass balance at the ice surface gives the following relationship:

$$
-\rho_{\rm w}c\frac{\partial p}{\partial r}\bigg|_{r=R+0} = \rho_{\rm i}V_{\rm i}\cos\theta
$$

The boundary conditions of the thermal and filtration problems involve an unknown velocity V_i , that needs to be defined from additional considerations.

Require the satisfiability of local thermodynamic equilibrium. At the phase interface, the chemical potential of water is equal to the chemical potential of ice. The standard expansion in series near the phase transition point of bulk water and ice results in the generalized Clapeyron–Clausius equation:

$$
\Delta P_{ik}/\rho_i - \Delta p_R/\rho_w = -\kappa \Delta t_R/T_0 \tag{3}
$$

where p_R , P_{iR} are the water pressure and the ice pressure component normal to an interface, t_R is the temperature at the inclusion surface, $T_0 = 273.15$ K. The values of P_{iR} , p_R , t_R are functions of the point's location on the surface.

Assume the external force fields to be absent. In this case only the surface forces act on the ice inclusion. One force of the disjoining pressure [\[7\]](#page-10-0) appears because of specific properties of water in the thin film and is perpendicular to interface. The other force of viscous friction is tangential to the surface and connected with the liquid flow around the inclusion. When the size of the inclusion is significantly greater than the layer thickness, the second force may be neglected in comparison with the first [\[8\].](#page-10-0) This supposition will be accepted in the future.

The ice velocity is constant in time, and therefore total force that acts on the inclusion surface S_R is equal to zero:

$$
\int_{S_R} P_{iR} d\mathbf{S} = 0 \tag{4}
$$

where $dS = n dS$; **n** is a unit vector perpendicular to dS .

Our intention is to determine the relationships between the fluxes through the cell and the temperature and pressure difference at its opposite sides. Those relations may be established after solving the system of Eqs. [\(1\) and \(2\)](#page-2-0) with [\(3\) and \(4\)](#page-2-0). The method of anisotropic conductivity [\[4\],](#page-9-0) which is used for solving that problem, allows us to find the required relationships and the transport coefficients in analytical form. The method is founded on the replacement of isotropic bodies by anisotropic elements and the application of the conservation and transfer laws in their initial forms.

It is assumed that in the direction of the Z-axis the properties of the medium are maintained to be real, and in the direction perpendicular to the external gradients the thermal and filtration coefficients are taken to be equal to zero or infinity. Solving the heat and mass transfer problem for two cells with different anisotropy, is a feature of this method. The transport coefficients of those cells give extreme values, which define the physically admissible region of variation. The transport coefficients of the cell with isotropic elements fall into that region.

3. Thermal problem

Laplace's equation (1) for temperature follows from two laws: the conservation of energy (heat balance) and Fourier's law

$$
\mathbf{j}_q = -\lambda \nabla t \tag{5}
$$

which states that the heat flux (j_q) is proportional to the temperature gradient ∇t .

These laws are used to define the stationary heat flux through a cell at constant temperatures on its bases (t_1) and t_2 [Fig. 2](#page-2-0)) and zero heat transfer through the lateral faces.

3.1. Infinite horizontal thermal conductivity

The temperature is constant at any horizontal section by virtue of the accepted anisotropy.

The medium is homogeneous in the intervals $-b/$ $2 < z < -R$ and $R < z < b/2$, the z-component of heat flux j_q does not depend on the z co-ordinate $(j_q = J_q)$ and therefore Fourier's law (5) reduces to the difference form:

$$
J_q = \lambda_2 \frac{t_1 - t'_1}{b/2 - R}
$$
 (6)

$$
J_q = \lambda_2 \frac{t'_2 - t_2}{b/2 - R} \tag{7}
$$

In the range of z from $-R$ to R the medium is heterogeneous and the heat is produced on the ice surface. Heterogeneity and presence of heat sources make to write the heat balance equation in integral form [\[9\]:](#page-10-0)

$$
\int_{\mathcal{S}} \mathbf{j}_q \, \mathrm{d} \mathbf{S} = \int_V I_q \, \mathrm{d} V \tag{8}
$$

where V is a volume enclosed by a surface of area S .

The physical meaning of last equation shines through—the total amount of heat leaving the volume equals the amount of heat produced by internal sources.

In order to define an equation for temperature on $z \in [-R, R]$, at first the heat balance will be written for a thin horizontal layer Δz (Fig. 3). In the system considered, the heat sources do not distribute all over the volume, but localize on the ice surface. Therefore the total heat production ΔQ_V in the layer Δz results in the ice– water phase transition on surface ΔS_R and is expressed in terms of the ice velocity relative to the mineral framework V_i (at $V_i > 0$ and $z > 0$ the ice melts with heat absorption)

$$
\Delta Q_{\rm V} = -\kappa \rho_{\rm i} \mathbf{V}_{\rm i} \mathbf{n}_{\rm R} \Delta S_{\rm R} = -\kappa \rho_{\rm i} V_{\rm i} z \Delta S_{\rm R} / R \tag{9}
$$

where n_R is a unit vector perpendicular to ΔS_R .

Denote by ΔQ_S the left-hand integral of Eq. (8). The quantity of heat ΔQ_s , which passes the surface of the selected layer, is the following:

$$
\Delta Q_{\rm S} = j_{12} S_{12} + j_{22} S_{22} - j_{11} S_{11} - j_{21} S_{21} \tag{10}
$$

where j_{kl} is the z-component of heat flux through corresponding area S_{kl} . The first index denotes the medium and the second—the surface of the selected volume.

Equating (9) and (10), representing area ΔS_R and S_{kl} as functions of R, z, Δz and then transforming to differential form gives an equation for z-components of fluxes j_{q1} and j_{q2} in elements E₁ and E₂:

$$
\frac{d j_{q2}}{dz} (S_a - \pi (R^2 - z^2)) + \frac{d j_{q1}}{dz} \pi (R^2 - z^2) \n+ (j_{q2} - j_{q1}) 2\pi z = -2\pi \kappa \rho_i V_i z
$$
\n(11)

Fig. 3. Heat transfer in the cell with infinite horizontal conductivity.

Using the Fourier's law: $j_{q1} = -\lambda_1 \frac{dt}{dz}$, $j_{q2} = -\lambda_2 \frac{dt}{dz}$ converts Eq. [\(11\)](#page-3-0) to an equation for temperature:

$$
-\frac{\mathrm{d}^2 t}{\mathrm{d}z^2}[\lambda_2 S_a + \pi(\lambda_1 - \lambda_2)(R^2 - z^2)] + \frac{\mathrm{d}t}{\mathrm{d}z}2\pi(\lambda_1 - \lambda_2)z
$$

= -2\pi\kappa\rho_i V_i z (12)

Thermal conductivity coefficients for soil are ordinarily less than for ice $(\lambda_2 < \lambda_1)$. Integrating Eq. (12) with the boundary conditions $t(-R) = t'_1$; $t(R) = t'_2$ gives a function for temperature distribution in the range of z from $-R$ to R:

$$
t(z) = \frac{\kappa \rho_1 V_1}{\Delta \lambda_{21}} z + \left(\frac{t'_2 - t'_1}{2R} - \frac{\kappa \rho_1 V_1}{\Delta \lambda_{21}} \right) \frac{R \ln \left| \frac{e_t + z}{e_t - z} \right|}{\ln \left| \frac{e_t + R}{e_t - R} \right|} + \frac{t'_2 + t'_1}{2}
$$
\n(13)

where $\Delta \lambda_{21} = \lambda_2 - \lambda_1$, e_t is defined from the following equation: $e_t^2 = \frac{\lambda_2 S_a - \Delta \lambda_{21} \pi R^2}{\pi |\Delta \lambda_{21}|}$.
At the boundary $z = \pm R$ heat fluxes need to be

continuous:

$$
-\lambda_2 \frac{\mathrm{d}t}{\mathrm{d}z}\bigg|_{z=\pm R} = J_q
$$

Substituting in the last equation the function $t(z)$ (13) gives following relationship:

$$
J_q = -\lambda_2 \left[\frac{\kappa \rho_i V_i}{\Delta \lambda_{21}} + \left(\frac{t'_2 - t'_1}{2R} - \frac{\kappa \rho_i V_i}{\Delta \lambda_{21}} \right) \frac{2e_i R}{\ln \left| \frac{e_i + R}{e_i - R} \right| (e_i^2 - R^2)} \right]
$$
(14)

Assuming in the set of Eqs. [\(6\), \(7\), and \(14\)](#page-3-0) the values t'_1 , t'_2 , J_q as unknown and solving them leads to the required heat flux J_a :

$$
J_q = \lambda_2 \left\{ -\frac{\kappa \rho_i V_i}{\Delta \lambda_{21}} - \left[\frac{t_2 - t_1}{b} - \frac{\kappa \rho_i V_i}{\Delta \lambda_{21}} \right] \cdot \frac{f_1}{\beta + f_1 (1 - \beta)} \right\},\tag{15}
$$

which includes the unknown velocity of ice V_i . For defining that, the distribution of temperature t_R on ice surface will be required. Substituting values t'_1 and t'_2 , previously found from the set (6) , (7) , and (14) , in Eq. (13) gives at $z = R\cos\theta$ that distribution:

$$
t_R(\theta) = \frac{\kappa \rho_i V_i}{\Delta \lambda_{21}} R \cos \theta
$$

+
$$
\left(\frac{t_2 - t_1}{b} - \frac{\kappa \rho_i V_i}{\Delta \lambda_{21}}\right) \frac{R}{\beta + f_1(1 - \beta)} \frac{\ln \left|\frac{1 + \varepsilon_i \cos \theta}{1 - \varepsilon_i \cos \theta}\right|}{\ln \left|\frac{1 + \varepsilon_i}{1 - \varepsilon_i}\right|} + t_0
$$

where $t_1 = \frac{t_2 + t_1}{\beta} = \frac{2R}{\beta}$, $\varepsilon_2 = R/\varepsilon$, $\varepsilon_1 = \frac{2\varepsilon_i}{\beta}$ (16)

where $t_0 = \frac{t_2 + t_1}{2}$, $\beta = 2R/b$, $\varepsilon_t = R/e_t$, $f_1 = \frac{2\varepsilon_t}{(1 - \varepsilon_t^2) \ln |\frac{1 + \varepsilon_t}{1 - \varepsilon_t}|}$.

The thermal problem is not yet solved finally. The relationship for heat flux J_q (15) includes an unknown velocity V_i .

3.2. Zero horizontal thermal conductivity

At zero horizontal conductivity the streamlines of heat flow are parallel to the Z-axis. Specify the polar co-ordinates (r, z) and coincide the point of origin with the centre of the cavity. In the range $r > R$ the medium is homogeneous (Fig. 4), the z-component of heat flux does not depend on the co-ordinate r and the value of the flux is defined from Fourier's law (5) :

$$
J_{q2} = -\lambda_2 \frac{t_2 - t_1}{b} \tag{17}
$$

Within the cylinder $r \le R$ the medium is heterogeneous and the heat sources are present. Consider a thin cylindrical layer Δr , which consists of three homogeneous parts on the co-ordinate z: $[-b/2,-h_1/2]$, $[-h_1/2]$ 2, $h_1/2$], $[h_1/2, b/2]$. Heat sources concentrate on the surfaces ΔS_R . On the upper surface with co-ordinate $z = +h₁/2$ heat is absorbed because of ice melting. On the lower surface with $z = -h_1/2$ the heat is extracted because of the water freezing. The total heat effect of both sources is equal to zero. Therefore heat fluxes in the upper and lower element E_2 are identical (J_{q1}) . The value of heat flux in every column (lower, middle, upper) of the layer is connected with temperature at their boundaries:

$$
J_{q1} = \lambda_2 \frac{t_1 - t_1'}{h_2}; \quad j_{q1} = \lambda_1 \frac{t_1' - t_2'}{h_1}; \quad J_{q1} = \lambda_2 \frac{t_2' - t_2}{h_2}
$$
\n(18)

where h_1 and h_2 are heights of columns E_1 and E_2 in the selected layer (Fig. 4).

The relation between heat fluxes in the elements E_1 and E_2 is found from the heat balance, taking into account the heat effect of the ice–water phase transition:

$$
j_{q1} - J_{q1} = \kappa \rho_i V_i \tag{19}
$$

Fig. 4. Heat transfer in the cell with zero horizontal conductivity.

Solving the system of Eqs. [\(18\) and \(19\)](#page-4-0) with respect to the values of j_{q1} , J_{q1} , t'_1 and t'_2 gives the relationships for the desired parameters:

$$
J_{q1} = \frac{\lambda_1 \lambda_2}{\lambda_1 h_1 + 2\lambda_2 h_2} \left(t_1 - t_2 - \kappa \rho_1 \frac{h_1}{\lambda_1} V_1 \right)
$$
 (20)

$$
t'_{k} = \frac{(-1)^{k} \lambda_{2} h_{1}}{\lambda_{1} h_{1} + 2\lambda_{2} h_{2}} \left(\frac{t_{2} - t_{1}}{2} - \kappa \rho_{1} \frac{h_{2}}{\lambda_{2}} V_{1}\right) + t_{0}, \quad k = 1, 2
$$
\n(21)

The temperatures t'_1 and t'_2 in Eq. (21) define the distribution of temperature t_R on the inclusion surface. Expressing heights h_1 and h_2 as functions of the radius R and an angle θ in Eq. (21) gives a function t_R :

$$
t_R(\theta) = \frac{\lambda_2 R \cos \theta}{\lambda_1 (1 + \varepsilon_0 \mid \cos \theta \mid)}
$$

$$
\times \left(\nabla_b t - \kappa \rho_i \frac{(1 - \beta \mid \cos \theta \mid)}{\lambda_2} V_i \right) + t_0
$$
 (22)

where $\varepsilon_0 = \beta \Delta \lambda_{21} / \lambda_1$, $\nabla_b t = (t_2 - t_1) / b$.

Before solving the second part of the thermal problem of defining the heat flow through the cell there is a need to remark that the value of the flux J_{q1} in range $r < R$ depends on the co-ordinate r. An explicit form for J_{q1} follows from Eq. (20) after substituting values h_1 and h_2 as functions of r and R:

$$
J_{q1}(r) = \frac{\lambda_1 \lambda_2}{b\lambda_1 + 2(\lambda_2 - \lambda_1)\sqrt{R^2 - r^2}} \times \left(t_1 - t_2 - \kappa \rho_i \frac{2\sqrt{R^2 - r^2}}{\lambda_1} V_i\right)
$$
(23)

An average heat flux J_q through the cell is defined as a ratio of total heat flux Q to the base area S_a :

$$
J_q = Q/S_a \tag{24}
$$

The known fluxes J_{q1} and J_{q2} (Eqs. (23) and (17)) make possible finding the total heat flux Q . Substituting Q in Eq. (24) gives:

$$
J_q = -\lambda_2 I_3 \nabla_b t - \alpha \beta \kappa \rho_i \lambda_2 V_i I_1 / \lambda_1 \tag{25}
$$

where $\alpha = \pi R^2 / S_a$, $I_1 = \frac{1}{\epsilon_0} \frac{2}{\epsilon_0^2}$ $\frac{2}{\epsilon_0^3} \ln(1+\epsilon_0), I_3 = (1-\alpha) +$ $\frac{2\alpha}{\epsilon_0^2}$ [$\epsilon_2 - \ln(1 + \epsilon_0)$].

An effective thermal conductivity coefficient is not found from the formula (25) because of that contents as before (see Eq. [\(15\)](#page-4-0)) an unknown velocity V_i .

Further actions purpose two objects to exclude the velocity V_i from Eqs. [\(15\) and \(25\)](#page-4-0) and to connect heat flux through the cell with the temperature at its bases. Realization of those intentions includes the following two steps: solving the filtration problem and finding the velocity of ice using conditions of the mechanical balance of the inclusion and the local thermodynamic equilibrium of ice and water.

4. Filtration problem

The filtration problem will be solved for the separated cell as follows: it is necessary to find the water flux through the cell at the prescribed pressure on the bases and in the absence of water flow through the lateral faces. The availability of liquid sources because of the ice–water phase transition must be taken into account while solving this problem. The overall arrangement of elements and fluxes is shown in [Fig. 2.](#page-2-0) The framework of the medium is assumed to be rigid. The components: water, ice and mineral are incompressible. Their densities and the hydroconductivity coefficient of the finepore part $E₂$ are constants.

The method of anisotropic conductivity will be used in order to solve the hydrodynamical problem as well as for thermal problem. This method is based on the substitution of anisotropic elements in place of the isotropic ones.

The mathematical part of the problem proposes to use the equation of mass continuity and Darcy's law, which specifies a connection between the liquid flux j_w and the pressure gradient:

$$
\mathbf{j}_{\mathbf{w}} = -c \nabla p \tag{26}
$$

Liquid migrates only in the element E_2 [\(Fig. 2\)](#page-2-0). Ice is impermeable for water.

All steps of finding the water flux through the cell replicate the chain of arguments in the solution of the thermal problem.

4.1. Infinite horizontal hydraulic conductivity

In the range of $z \in [-b/2,-R]$ and $[R,b/2]$ the medium is homogeneous and Darcy's law (26) may be written in the different forms:

$$
J_{\rm w} = c \frac{p_1 - p_1'}{b/2 - R} \tag{27}
$$

$$
J_{\rm w} = c \frac{p_2' - p_2}{b/2 - R} \tag{28}
$$

where p'_1 and p'_2 are pressures at sections $z = -R$ and R respectively; J_w is the water flux through the bases of the cell.

In the region $z \in [-R, R]$ the filtration problem will be solved analogously to the thermal problem in Section 2.1. Select a horizontal layer with a thickness of Δz [\(Fig.](#page-6-0) [5](#page-6-0)) and write the condition of mass balance. Present the conservation of mass for a multiphase medium in a stationary process by the integrated forms [\[10\]](#page-10-0):

Fig. 5. Mass transfer in the cell with infinite horizontal conductivity.

$$
\int_{S} \rho_{i} n_{i} \mathbf{V}_{i} d\mathbf{S} = \int_{V} I_{\text{wi}} dV
$$
\n(29)

$$
\int_{S} \rho_{\mathbf{w}} n_{\mathbf{w}} \mathbf{v}_{\mathbf{w}} d\mathbf{S} = \int_{V} I_{\text{iw}} dV \tag{30}
$$

where I_{kl} is an antisymmetric function:

$$
I_{kl} = -I_{lk} \tag{31}
$$

Summing Eqs. (29) and (30) having in view (31), leads to the following equation for mass balance

$$
\rho_{\rm i} \int_S n_{\rm i} V_{\rm i}^n \, \mathrm{d}S + \rho_{\rm w} \int_S n_{\rm w} v_{\rm w}^n \, \mathrm{d}S = 0 \tag{32}
$$

Applying Eq. (32) to the layer Δz , converting to the differential form ($\Delta z \rightarrow 0$) and taking into account relation $j_w = n_w v_w$ gives the differential equation for the z-component of water flux j_{wz} :

$$
\frac{d j_{wz}}{dz} \left(\frac{S_a}{\pi} - R^2 + z^2 \right) + 2z j_{wz} = \frac{2z \rho_i V_i}{\rho_w}
$$

Substituting the value j_{wz} from Eq. [\(26\)](#page-5-0) in the last equation transforms that to an equation for water pressure:

$$
\frac{d^2 p}{dz^2} \left(\frac{S_a}{\pi} - R^2 + z^2 \right) + 2z \frac{dp}{dz} = -\frac{2z \rho_i V_i}{\rho_w c}
$$
(33)

Solving Eq. (33) with boundary conditions: $p(-R) = p'_1$; $p(R) = p'_2$ gives a dependence of a value of p on co-ordinate z :

$$
p(z) = -\frac{\rho_i V_i}{\rho_w c} z + \left(\frac{p'_2 - p'_1}{2R} + \frac{\rho_i V_i}{\rho_w c}\right) \frac{R \arctg\left(\frac{z}{e_p}\right)}{\arctg(e_p)} + \frac{p'_2 + p'_1}{2}
$$
(34)

where $e_p^2 = \frac{S_a - \pi R^2}{\pi}$; $\varepsilon_p = \frac{R}{e_p}$.

The condition of mass continuity at sections $z = \pm R$ results in the following relationship:

$$
J_{\rm w} = -c \frac{\mathrm{d}p}{\mathrm{d}z} \bigg|_{z=\pm R}
$$

Substituting in the last equation the function $p(z)$ (34) gives:

$$
J_{\rm w} = \frac{\rho_{\rm i} V_{\rm i}}{\rho_{\rm w}} - \left(c \cdot \frac{p_2' - p_1'}{2R} + \frac{\rho_{\rm i} V_{\rm i}}{\rho_{\rm w}} \right) \frac{\varepsilon_p}{(1 + \varepsilon_p^2) \arctg(\varepsilon_p)} \tag{35}
$$

Solving the set [\(27\), \(28\), and \(35\)](#page-5-0) with respect to the unknown values of p'_1 , p'_2 and J_w leads to an explicit form for water flux:

$$
J_{\rm w} = \frac{\rho_{\rm i} V_{\rm i}}{\rho_{\rm w}} - \left(c \cdot \nabla_b p + \frac{\rho_{\rm i} V_{\rm i}}{\rho_{\rm w}} \right) \frac{f_2}{\beta + f_2 (1 - \beta)}\tag{36}
$$

where $\nabla_b p = \frac{p_2 - p_1}{b}$; $f_2 = \frac{\varepsilon_p}{(1 + \varepsilon_p^2) \arctg(\varepsilon_p)}$ The relation (36) includes an unknown velocity of ice V_i , which needs to be defined separately. For that it is necessary to know a pressure distribution p_R around the ice inclusion. Finding the values p'_1 and p'_2 from the system [\(27\), \(28\), and](#page-5-0) [\(35\)](#page-5-0) and substituting those in Eq. (34) gives at $z = R\cos\theta$ a desired function $p_R(\theta)$:

$$
p_R(\theta) = -\frac{\rho_i V_i}{\rho_w c} R \cos \theta + \left(\nabla_b p + \frac{\rho_i V_i}{\rho_w c}\right) \frac{R}{\beta + f_2 (1 - \beta)} \cdot \frac{\text{arctg}(\varepsilon_p \cos \theta)}{\text{arctg}(\varepsilon_p)} + p_0
$$
(37)

where $p_0 = (p_1 + p_2)/2$.

4.2. Zero horizontal hydraulic conductivity

At zero horizontal conductivity the lines of water flow are parallel to Z-axis.

In the region $r > R$ the medium is homogeneous [\(Fig.](#page-7-0) [6](#page-7-0)), water flux does not depend on polar co-ordinate r and Darcy's law [\(26\)](#page-5-0) converts to difference form:

$$
J_{w2} = -c\frac{p_2 - p_1}{b} \tag{38}
$$

within a cylinder where $r \le R$, the medium is heterogeneous and phase transition occurs on the surface of ice inclusion. Select in the cell a thin cylindrical layer Δr , which consists of three uniform columns on co-ordinate z: $[-b/2,-h₁/2]$, $[-h₁/2,h₁/2]$, $[h₁/2,b/2]$ [\(Fig. 6\)](#page-7-0). Phase transition and liquid production take place on the upper and lower surfaces ΔS_R of the middle column. In a stationary process the water flows in the outer columns are equal to J_{w1} . The value of water flux connects with ice velocity V_i in accordance with the conservation of mass:

$$
\rho_{\rm w} J_{\rm w1} = \rho_{\rm i} V_{\rm i} \tag{39}
$$

The last equation shows that the value of the flux J_{w1} is constant all over the region $r \le R$ and therefore does not depend on co-ordinate r .

Fig. 6. Mass transfer in the cell with zero horizontal conductivity.

The total water flux M through the bases of the cell is expressed in the terms J_{w1} and J_{w2} :

$$
M = J_{w1}\pi R^2 + J_{w2}(S_a - \pi R^2)
$$
\n(40)

By definition, the average water flux is the ratio of water discharge to area:

$$
J_{\rm w} = M/S_{\rm a} \tag{41}
$$

Substituting the value of M (40) in Eq. (41) and excluding fluxes $J_{\rm w2}$ and $J_{\rm w1}$ by means of [\(38\) and \(39\)](#page-6-0) gives a desired relationship for J_w as a function of pressure gradient and ice velocity:

$$
J_{\rm w} = \frac{\rho_{\rm i}}{\rho_{\rm w}} \alpha V_{\rm i} - (1 - \alpha)c \nabla_b p \tag{42}
$$

The ice velocity will be defined in the future, but that requires knowledge of pressure distribution at the surface of the ice inclusion. Applying Darcy's law to the outer columns of the layer Δr gives:

$$
J_{\rm w1} = c \frac{p_1 - p_1'}{h_2} \tag{43}
$$

$$
J_{\rm w1} = c \frac{p_2' - p_2}{h_2} \tag{44}
$$

where h_2 is the height of column E_2 in the selected layer (Fig. 6).

The values of p'_1 and p'_2 are the distribution of pressure p_R at the inclusion surface. Expressing h_2 as a function of the radius R and an angle θ and substituting J_{w1} from [\(39\)](#page-6-0) in (43) and (44) gives a function $p_R(\theta)$:

$$
p_R(\theta) = p_k + (-1)^k \frac{\rho_i R}{\rho_w \beta} V_i \frac{1 - \beta |\cos \theta|}{c},
$$

$$
\begin{cases} k = 2, & 0 \le \theta < \pi/2\\ k = 1, & \pi/2 \le \theta \le \pi \end{cases}
$$
 (45)

5. Velocity of ice and transfer equations

Consider two anisotropic media. The first holds the highest possible conductive properties: the horizontal thermal and hydraulic conductivities are infinite. The second has minimal horizontal conductivities.

The symmetry of the solution (see (16) , (22) , (37) , [\(45\)](#page-4-0)) and Eq. [\(3\)](#page-2-0) convert the integral [\(4\)](#page-2-0) to the following form:

$$
\frac{\rho_{\rm i}}{\rho_{\rm w}} \int_0^{\pi} p_R(\theta) \cos \theta \sin \theta \, \mathrm{d}\theta - \frac{\kappa \rho_{\rm i}}{T_0} \int_0^{\pi} t_R(\theta) \cos \theta \sin \theta \, \mathrm{d}\theta = 0 \tag{46}
$$

The last relationship realizes the conditions of the mechanical balance of the ice and the local thermodynamical equilibrium in the system.

5.1. Infinite horizontal conductivities

Substituting the Eqs. [\(16\) and \(37\)](#page-4-0) in Eq. (46) enables us to produce the ice velocity as a linear function of the temperature and pressure gradients along the height of the cell:

$$
V_{i} = \frac{\kappa \rho_{i}}{T_{0}} \frac{f_{t}}{D} \nabla_{b} t - \frac{\rho_{i}}{\rho_{w}} \frac{f_{p}}{D} \nabla_{b} p
$$
(47)
where $f_{t} = \frac{(1-f_{1})(\varepsilon_{t}^{2}-1)}{[\beta+(1-\beta)f_{1}]\varepsilon_{t}^{2}};$ $f_{p} = \frac{(1-f_{2})(1+\varepsilon_{p}^{2})}{[\beta+(1-\beta)f_{2}]\varepsilon_{p}^{2}};$ $D = \left(\frac{\rho_{i}}{\rho_{w}}\right)^{2} \frac{(f_{p}-2/3)}{c} + \frac{(\kappa \rho_{i})^{2}(f_{t}-2/3)}{T_{0}\Delta z_{1}}.$

Substituting the value of the ice velocity V_i from Eq. (47) in Eqs. [\(15\) and \(36\)](#page-4-0) gives the explicit form for the heat and water flux through the cell. Omitting all intermediate conversions, the final result is following:

$$
J_q = -C_{qq}\nabla_b t - C_{qw}\nabla_b p \tag{48}
$$

$$
J_{\rm w} = -C_{\rm wq} \nabla_b t - C_{\rm ww} \nabla_b p \tag{49}
$$

with the transport coefficients to be equal

$$
C_{qq} = \lambda_2 \left[f_q + \frac{(\kappa \rho_1)^2}{T_0 \Delta \lambda_{21}} \cdot \frac{f_l (1 - f_q)}{D} \right]
$$
 (50)

$$
C_{qw} = -\frac{\lambda_2 \kappa \rho_1^2}{\Delta \lambda_{21} \rho_w} \cdot \frac{(1 - f_q)f_p}{D} \tag{51}
$$

$$
C_{\rm ww} = c \left[f_{\rm w} + \left(\frac{\rho_{\rm i}}{\rho_{\rm w}} \right)^2 \frac{(1 - f_{\rm w}) f_p}{c D} \right]
$$
 (52)

$$
C_{\text{wq}} = -\frac{\kappa \rho_{\text{i}}^2}{\rho_{\text{w}} T_0} \cdot \frac{(1 - f_{\text{w}}) f_t}{D} \tag{53}
$$

where $f_q = \frac{f_1}{\beta + (1 - \beta)f_1}$; $f_w = \frac{f_2}{\beta + (1 - \beta)f_2}$.

Therefore heat and mass transfer in the model porous medium with ice is described by the set of Eqs. (48) and (49). The transport coefficients depend on the parameters λ_1 , λ_2 , c, α , β ; those characterize the thermal and mass properties of the medium and its geometric configuration.

We must check that the transport coefficients are in agreement with Onsager's reciprocal relations. For that, the thermodynamical forces X_w and X_q , which correspond to mass and heat fluxes, need to be presented in terms of nonequilibrium thermodynamics [\[11\]](#page-10-0): $X_w =$ $\nabla_b p/\rho_w$, $X_q = \nabla_b t/T_0$ and the flux of the substance must be written as the mass flow: $J_{\text{m}} = \rho_{\text{w}} J_{\text{w}}$.

In the result, the equations of the heat and mass transfer reduce to the following form:

$$
J_q = -\widetilde{C}_{qq} X_q - \widetilde{C}_{qw} X_w \tag{54}
$$

$$
J_{\rm m} = -\widetilde{C}_{\rm wq} X_q - \widetilde{C}_{\rm ww} X_{\rm w} \tag{55}
$$

New coefficients in Eqs. (54) and (55) are connected with the old ones [\(50\) and \(53\)](#page-7-0) by the following relations:

$$
\widetilde{C}_{qq} = C_{qq} T_0; \quad \widetilde{C}_{qw} = C_{qw} \rho_w; \n\widetilde{C}_{wq} = C_{wq} \rho_w T_0; \quad \widetilde{C}_{ww} = C_{ww} \rho_w^2
$$
\n(56)

Appropriate algebraic manipulations produce a formula for nondiagonal coefficients:

$$
\widetilde{C}_{qw} = \widetilde{C}_{wq} = -\frac{\lambda_2 \kappa \rho_1^2}{\Delta \lambda_{21}} \cdot \frac{1}{\alpha \beta} \frac{(1 - f_q)(1 - f_w)}{D}
$$

The symmetry of the transport coefficients on the one hand gives promise that the problem statement about heat and mass transfer is correct, but, on the other hand, shows that the postulates of nonequilibrium thermodynamics appear to be valid in the region of phase transition. The values of all coefficients are of the same order of magnitude.

5.2. Zero horizontal conductivities

In the cell with zero horizontal mass and thermal conductivity, the distributions of temperature and pressure at the boundary of the ice are defined by functions [\(22\) and \(45\).](#page-5-0) Substituting those in Eq. [\(46\)](#page-7-0) and subsequent algebraic manipulations result in a relation for ice velocity as a linear function of temperature and pressure gradients:

$$
V_{\rm i} = \frac{\kappa \rho_{\rm i} \lambda_2}{T_0 \lambda_1} \frac{I_1}{D^0} \nabla_b t - \frac{\rho_{\rm i}}{\rho_{\rm w} \beta} \frac{1}{D^0} \nabla_b p \tag{57}
$$

where $D^0 = (1 - \frac{2}{3}\beta)(\frac{\rho_1}{\rho_w})^2 \frac{1}{\beta_c} + \frac{(\kappa \rho_1)^2}{\lambda_1 T_0} (I_1 - \beta I_2); I_2 = \frac{2}{3\epsilon_0} - \frac{1}{\epsilon_0^3} + \frac{2}{\epsilon_0^3} - \frac{2}{\epsilon_0^4} \ln(1 + \epsilon_0).$

Substituting Eq. (57) in Eqs. [\(25\) and \(42\)](#page-5-0) gives a linear dependence of heat and mass fluxes on gradients of temperature and pressure in form [\(48\) and \(49\)](#page-7-0) with transport coefficients as follows:

$$
C_{qq}^{0} = \lambda_2 I_3 + \frac{\alpha \beta (\lambda_2 \kappa \rho_1)^2}{\lambda_1^2 T_0} \cdot \frac{I_1^2}{D^0}
$$
 (58)

$$
C_{qw}^{0} = C_{wq}^{0} T_0 = -\frac{\alpha \lambda_2 \kappa \rho_1^2}{\lambda_1 \rho_w} \cdot \frac{I_1}{D^0}
$$
 (59)

$$
C_{\text{ww}}^0 = (1 - \alpha)c + \frac{\alpha}{\beta} \left(\frac{\rho_i}{\rho_{\text{w}}}\right)^2 \frac{1}{D^0}
$$
 (60)

At zero horizontal conductivities the standard cross coefficients turn out also to be equal as that follows from (59) and (56).

6. Effective thermal conductivity of porous medium with heat dipoles

The value of heat flux through the cell depends on not only the gradient temperature, but also on the gradient of pressure [\(47\)](#page-7-0). That comes from the essential effect of pressure gradients on ice movement in a cavity. As soon as the defined limitations are imposed on a pressure gradient, it may be said about effective coefficient of thermal conductivity. Consider two routine systems—closed and open. In an open system, the pressure drop per the height of the cell is equal to zero $(p_1 = p_2)$. In this case the heat transfer will be accompanied by mass transfer.

The value of effective thermal conductivity λ_0 of an open system follows from Eq. [\(48\)](#page-7-0) at $\nabla_b p = 0$:

$$
\widetilde{\lambda}_{\text{O}0} = C_{qq}^0; \quad \widetilde{\lambda}_{\text{O}1} = C_{qq}
$$

where inferior indices of 0 and 1 designate a medium with zero and infinite horizontal conductivities accordingly.

In closed system the mass flow through the cell equals zero ($J_w = 0$). Using relation [\(49\)](#page-7-0) for defining pressure gradients and substituting that equation in [\(48\)](#page-7-0) gives a value of effective coefficient of thermal conductivity of closed sample λ_c :

$$
\widetilde{\lambda}_{C0} = C_{qq}^{0} - \frac{T_0 (C_{\text{wg}}^{0})^2}{C_{\text{ww}}^{0}}, \quad \widetilde{\lambda}_{C1} = C_{qq} - \frac{T_0 C_{\text{wg}}^{2}}{C_{\text{ww}}}
$$

Coefficients $\tilde{\lambda}_0$ and $\tilde{\lambda}_c$ depend on all input parameters $(\lambda_1, \lambda_2, c, \alpha, \beta)$ including a hydroconductivity coefficient c of fine-pore medium E_2 .

Transfer parameters were calculated for a cubical cell, the elements of which $(E_1 \text{ and } E_2)$ hold the coefficients of the thermal conductivities, as follows: $\lambda_1 = 2.2 \,\mathrm{W} \,\mathrm{m}^{-1} \,\mathrm{K}^{-1}; \lambda_2 = 1.54 \,\mathrm{W} \,\mathrm{m}^{-1} \,\mathrm{K}^{-1}.$

Curves in [Fig. 7](#page-9-0) show that the value of the thermal conductivity grows with increasing the part by ice volume n in the cell (ratio of ice volume to cell volume) and hydroconductivity c of fine-pore medium E_2 . When $c < 10^{-15}$ m³s kg⁻¹ the value of the effective thermal conductivity becomes equal to the thermal conductivity of the system with immovable ice $(c = 0)$ and is scarely affected by hydraulic permeability of the medium. When

Fig. 7. Effective thermal conductivities of open (solid lines) and closed (dot lines) systems versus part by ice volume in the cubic cell at different hydroconductivity coefficients c of fine-pore medium (E_2) [m³skg⁻¹]: (1) 10^{-12} ; (2) 10^{-13} ; (3) 10^{-14} ; (4) 10^{-15} with zero (a) and infinite (b) horizontal conductivity.

 $c > 10^{-14}$ m³s kg⁻¹ the effective coefficient of thermal conductivity may be several times greater than the similar parameter for a system with immovable ice. Heatconducting properties of the medium increase noticeably because of the presence of the heat dipoles.

A comparison of curves in Fig. 7 shows that the thermal conductivity of an open system is always greater than that of a closed one. The ratio of effective coefficients of open/closed systems increases monotonically with increasing ice content and may amount to 1.5.

The intensity of heat dipoles depends on the ice contents and hydraulic conductivity of the porous medium. In real frozen soil, the intensity has a maximum near the freezing-point temperature. Explorations of thermophysical properties of frozen soil display maximum of the thermal conductivity coefficient vs. temperature [\[12\]](#page-10-0). An observed maximum of the curve may be explained by working of heat dipoles.

In addition, the value of the thermoosmosis coefficient $\chi = C_{wa}/\rho_w$ is adduced to confirm unique properties of the considered system. For example, at the values of $n = 0.4$; $c = 10^{-13} \text{ m}^3 \text{ s kg}^{-1}$ and the same for the remaining parameters, the coefficient γ is about 10^{-6} m²s⁻¹. This result is six orders of magnitude greater than the value of the thermoosmosis coefficient which is derived in experiments with a porous medium been saturated a single-phase substance [\[13\].](#page-10-0)

7. Conclusions

In porous media with phase transitions, the heat and mass transfer laws have to be presented in a generalized form [\(54\) and \(55\)](#page-8-0).

Cross effects in media with phase transition are significantly greater than in media with a single-phase filling substance.

Intensification of cross effects comes out from the regelation movement of solid (ice).

Transport coefficients near the freezing-point temperature reach a maximum.

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