

Development of Mathematical Model of Heat and Mass Transfer in Soil, with Provision for the Gradients of soil-water and soil-salt potentials. Part 2

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Abstract.

The article is devoted to mathematical modeling of heat and mass transfer in soil. The construction of different structures on heaving soils requires verification of their stiffness. Frost heaving comes with water displacement from the thawed to freezing soil and ice segregation. This process is only possible in a non-equilibrium conditions. To describe the movement patterns of interstitial solution, most scientists use the generalized thermodynamic laws based on the action of all the thermodynamic driving forces. Without the using of non-equilibrium thermodynamics laws, this approach does not allow to identify the link between kinetic coefficient determined by different mechanisms.

In the first part of this article, the authors proved that the potential of all components of water-salt solution in soil may consist of the chemical potential and the potential of external volume forces, which are non-zero. Also in the first part the authors derived the equation of the dynamics of pore solution, which takes into account the gradients of decreasing the potential of all components of solution in soils.

In second part of the article, the authors used the equation of pore solution dynamics and the conclusions of the first part to develop a mathematical model of heat and mass transfer in soils. The equation of the speed of changing of kinetic energy, potential energy, sorption energy, internal energy and total energy conservation, potential energy conservation and total energy was written. With the help of the second law of thermodynamics, the equation for the transfer of entropy is written. Onsager theorem and volume source of entropy allowed to write the equations for thermodynamic driving forces and flows with allowance for cross effects.

Keywords: frost heaving, Onsager reciprocal relations, thermodynamic driving forces and flows, all components capillary-sorption gradients

INTRODUCTION

The field of application of mathematical models of heat and mass transfer is a description of the dynamics of the heaving soils. This soils have a significant influence on the stability of different constructions [1 - 4]. Frost heaving is a process that develops under non-equilibrium conditions, which provoke the water flow from thawed to frozen soil. However, the dynamics of pore solution is determined not only by the temperature gradient, but also by the gradients of the capillary-sorption potentials and the concentrations of all components of the water-salt solution and pressure. It was shown in the first part of this article [5]. The most authors use generalized thermodynamic laws based on the action of thermodynamic driving forces to describe the regularities of this displacement of pore solution [6, 7]. This approach does not allow to reveal the relationships between transfer coefficients determined by different mechanisms without the application of the laws of nonequilibrium thermodynamics.

Quite often, the models do not take into account the capillary-sorption potentials [8], or separate sorption-desorption flow, that only increase in the number of experimentally determined parameters [9].

OBJECT AND PURPOSE

In the second part of the article the authors solved the following problem:

- to derive mathematical model of heat and mass transfer, taking into account the gradients of capillary-sorption potentials and concentrations of all components, temperature and pressure gradients based on the linear non-equilibrium thermodynamics and Onsager reciprocal relations [10].

RESEARCH METHOD

Authors derived next equation to construct mathematical model of heat and mass trans-fer:

1. Equation of the solution dynamics and the equation of the changing rate of kinetic en-ergy density for solution and gas mixture
2. Equation of the changing rate of potential, internal and total energy density for solu-tion and gas mixture.
3. Equation of the changing rate of sorption energy density for solution additionally.
1. This equation is necessary to describe the energy associated with the capillary sorption forces acting on the molecules of the water-salt solution in the soils. Influence of these forces becomes significant in finely-divided systems with huge specific surface area, for exam-ple soils.
4. Entropy transfer equation, using the second law of thermodynamics.
5. Systems of the equations of thermodynamic driving forces and flows using Onsager reciprocal relations

In the third part of the article authors will evaluate each force of every flux and will de-rive expressions for the kinetic coefficients. Also authors will write the final equations of the non-stationary heat and mass transfer in the soil.

DERIVING THE SYSTEMS OF THE EQUATIONS OF THERMODYNAMIC DRIVING FORCES AND FLOWS

The mathematical model uses next hypothesis:

- it is assumed that, phenomenological laws are described by linear equations in some very small area, which is true for the most of transport phenomenon [11];
- mass transfer of components is possible only in liquid or gaseous phase. The transfer-ring rate of mineral particles of the soil skeleton is close to zero.
- the transfer of components in the gaseous phase is possible only under the influence of the pressure gradient and concentration;
- the interaction of the vapor and liquid phases is possible only in the evaporation-condensation processes. This assumption is justified by the Curie symmetry principle whereby flows and thermodynamic forces of different tensor dimension can not be communicated [10]. For example, evaporation has a tensor of zero rank, but all flows are vectors.
- the solution is always electrically neutral; i.e. the diffusion coefficients of the different ions of one molecule is equal. This allows us to exclude from consideration the cross effects of Peltier and Seebeck.
- the ions in the loosely associated part of the double electric layer predominate in the soil and the adsorbed

part is negligible in soil. This allow to neglect the effects of diffusion de-celeration and also to consider the transfer of salts in the soil just like in a free solution. This assumption is justified by the fact that the size of the adsorption layer does not exceed 10 nm, but only the pore size is more than 10 μm is important for frost heaving [7].

- the formation of a mineral skeleton of soil from the matter contained in pore space re-quires a geological time scale and is taken to be negligible.

In the first part of this article we have derived the following key equations:

$$\psi_i = \psi_i^{ch} + \psi_i^{evf}, \tag{1}$$

$$\sum_{i=1}^m (\omega_i d\psi_i^{xmm}) = 0, \tag{2}$$

$$\wp_{ws} \frac{d\vec{W}_{ws}}{dt} = -n_{ws} \nabla P - \wp_{ws} \sum_{i=1}^m \omega_i \nabla \psi_i + \wp_{ws} (\vec{a} + \vec{F}_{fr}^{ws}), \tag{3}$$

where ψ_i - decreasing of the potential of the i -th component in soil solution in comparison with free solution, J/kg; ψ_i^{evf} - part of ψ_i belong to potential of external volume forces, J/kg; ψ_i^{ch} - part of ψ_i , belong to chemical potential, J/kg; ω_i - mass concentration of the i -th component in solution; \wp_{ws} - content of water-salt solution in soil, kg/m³; \vec{W}_{ws} - vector of true solution velocity as a single body, m/s; n_{ws} - volume fraction of water-salt solution in the soil, u.f.; P - hydrostatic pressure, Pa; \vec{a} - external acceleration of the system, m/s²; \vec{F}_{fr}^{ws} - specific friction force acting on the water-salt solution, N/kg; m - number of components of water-salt solution.

From equations (1) - (3) we obtained the following conclusion:

$$\sum_{i=1}^m (\omega_i d\psi_i) = \sum_{i=1}^m (\omega_i d\psi_i^{evf}) \tag{4}$$

$$\wp_{ws} \frac{d\vec{W}_{ws}}{dt} = -n_{ws} \nabla P - \wp_{ws} \sum_{i=1}^m \omega_i \nabla \psi_i^{evf} + \wp_{ws} (\vec{a} + \vec{F}_{fr}^{ws}). \tag{5}$$

Then we wrote the equation of the rate of change in the kinetic energy density. To this end, we multiplied (5) by the velocity of the solution \vec{W}_{ws} and equated the external acceleration to the external conservative force $\vec{F}_i^{c,ws}$ (for example, gravity):

$$\frac{\partial \left(\frac{(\vec{W}_{ws})^2}{2} \wp_{ws} \right)}{\partial t} = -\nabla \cdot \left(\vec{W}_{ws} \wp_{ws} \frac{(\vec{W}_{ws})^2}{2} \right) - n_{ws} \vec{W}_{ws} \cdot \vec{\nabla} P - \vec{W}_{ws} \cdot \sum_{i=1}^m (\wp_{ws} \vec{W}_{ws} \nabla \psi_i^{evf}) + \vec{W}_{ws} \cdot \sum_{i=1}^m \wp_{ws} \vec{F}_i^{c,ws} + \vec{W}_{ws} \cdot \wp_{ws} \vec{F}_{rf}^{ws}, \tag{6}$$

where $\vec{F}_i^{c,ws}$ – specific conservative force acting on the i -th component of water-salt solution, N/kg; ρ_i^{ws} – content of i -component of water-salt solution in soil, kg/m³;

Then we wrote the similar equation for gas mixture in soil and we have taken into account that only the pressure gradient and mass forces act on the gas mixture:

$$\frac{\partial \left(\frac{(\overline{W}_{gm})^2}{2} \rho_{gm} \right)}{\partial t} = -\nabla \cdot \left(\overline{W}_{gm} \rho_{gm} \frac{(\overline{W}_{gm})^2}{2} \right) - n_{gm} \overline{W}_{gm} \cdot \vec{\nabla} P + \overline{W}_{gm} \cdot \sum_{l=1}^k \rho_l^{gm} \vec{F}_l^{c,gm} + \overline{W}_{gm} \cdot \rho_{gm} \vec{F}_{fr}^{gm}, \quad (7)$$

where ρ_{gm} – content of gas mixture solution in soil, kg/m³; \overline{W}_{gm} – vector of true gas mixture velocity as a single body, m/s; n_{gm} – volume fraction of gas mixture in the soil, u.f.; ρ_l^{gm} – content of l -component of gas mixture in soil, kg/m³; $\vec{F}_l^{c,gm}$ – specific conservative force acting on the l -th component of gas mixture, N/kg; \vec{F}_{fr}^{gm} – specific friction force acting on the gas mixture, N/kg; k – number of components in gas mixture.

Next, we wrote the equation of the rate of change in the potential energy density for the solution and the gas mixture:

$$\frac{\partial (\rho_{ws} \psi_M^{c,ws})}{\partial t} = -\nabla \cdot \left(\sum_{i=1}^m \rho_i^{ws} \overline{W}_i^{ws} \psi_i^{c,ws} \right) - \sum_{i=1}^m (\vec{j}_i^{ws} \cdot \vec{F}_i^{c,ws}) - \overline{W}_{ws} \cdot \sum_{i=1}^m (\rho_i^{ws} \vec{F}_i^{c,ws}); \quad (8)$$

$$\frac{\partial (\rho_{gm} \psi_M^{c,gm})}{\partial t} = -\nabla \cdot \left(\sum_{l=1}^k \rho_l^{gm} \overline{W}_l^{gm} \psi_l^{c,gm} \right) - \sum_{l=1}^k (\vec{j}_l^{gm} \cdot \vec{F}_l^{c,gm}) - \overline{W}_{gm} \cdot \sum_{l=1}^k (\rho_l^{gm} \vec{F}_l^{c,gm}), \quad (9)$$

where $\psi_M^{c,ws}$ – average mass potential of conservative forces of water-salt solution, J/kg; $\psi_i^{c,ws}$ – potential of conservative forces of the i -th component of the water-salt solution, J/kg; $\psi_M^{c,gm}$ – average mass potential of conservative forces of gas mixture, J/kg; $\psi_l^{c,gm}$ – potential of conservative forces of the l -th component of the gas mixture, J/kg; \vec{j}_i^{ws} – diffusion flux of the i -th component of water-salt solution, kg/(s·m²); \vec{j}_l^{gm} – diffusion flux of the l -th component of gas mixture, kg/(s·m²).

Except kinetic, potential and internal energy, in the water-salt solution exist sorption energy. To take into account sorption energy we derived the equation of the changing rate of sorption energy density with nonlinear dependence of sorption energy from content of i -th component of the water-salt solution in soil ρ_i^{ws} :

$$\psi_i^{ws} = \int_0^{\rho_i^{ws}} \psi_i d\rho_i^{ws}. \quad (10)$$

Because all the parameters entering into (2.30) depend on time in the fixed volume, the changing rate of sorption energy density in a stationary volume is expressed as the derivative of the integral with a variable upper limit:

$$\frac{\partial \psi_i^{ws}}{\partial t} = \psi_i^{evf} \frac{\partial \rho_i^{ws}}{\partial t} = -\psi_i^{evf} \nabla \cdot (\vec{j}_i^{ws} + \rho_i^{ws} \overline{W}_i^{ws}). \quad (11)$$

where ψ_i^{ws} – part of sorption energy density of external volume forces acting on i -th component of the water-salt solution, Дж/кг.

Summation of (11) over all components of water-salt solution gave us equation of the changing rate of sorption energy density:

$$\sum_{i=1}^m \frac{\partial \psi_i^{ws}}{\partial t} = \sum_{i=1}^m \left(-\nabla \cdot (\psi_i^{evf} \vec{j}_i^{ws} + \psi_i^{evf} \rho_i^{ws} \overline{W}_i^{ws}) \right) + \sum_{i=1}^m (\vec{j}_i^{ws} \cdot \vec{\nabla} \psi_i^{evf} + \rho_i^{ws} \overline{W}_i^{ws} \cdot \vec{\nabla} \psi_i^{evf}). \quad (12)$$

Next, we wrote the balance equation of total energy density. In our case total energy density consist of kinetic, potential, sorption and internal energy density. On the flipside, total energy density changes as the result of kinetic energy inflow, potential energy inflow, sorption energy inflow and heat inflow. We derived equation of the total energy density in the soil using well-known thermodynamic relations for the enthalpy, pressure and internal energy ($Q=U+PV$):

$$\frac{\partial \left(\rho_{ws} \left(\frac{(\overline{W}_{ws})^2}{2} + \psi_M^{c,ws} + u_{ws} \right) + \rho_{gm} \left(\frac{(\overline{W}_{gm})^2}{2} + \psi_M^{c,gm} + u_{gm} \right) \right)}{\partial t} + \frac{\partial (\rho_{sk} u_{sk} + \sum_{i=1}^m \psi_i^{evf})}{\partial t} = -\nabla \cdot (\vec{j}_q) - \nabla \cdot (\rho_{ws} u_{ws} \overline{W}_{ws} + n_{ws} P \overline{W}_{ws} + \sum_{i=1}^m h_i^{ws} \vec{j}_i^{ws}) - \nabla \cdot (\rho_{gm} u_{gm} \overline{W}_{gm} + n_{gm} P \overline{W}_{gm} + \sum_{l=1}^k h_l^{gm} \vec{j}_l^{gm}) - \nabla \cdot \left(\frac{(\overline{W}_{ws})^2}{2} \rho_{ws} \overline{W}_{ws} \right) - \nabla \cdot \left(\frac{(\overline{W}_{gm})^2}{2} \rho_{gm} \overline{W}_{gm} \right) - \nabla \cdot \left(\sum_{i=1}^m \rho_i^{ws} \overline{W}_i^{ws} \psi_i^{c,ws} \right) - \nabla \cdot \left(\sum_{l=1}^k \rho_l^{gm} \overline{W}_l^{gm} \psi_l^{c,gm} \right) - \nabla \cdot \left(\sum_{i=1}^m \psi_i^{evf} \vec{j}_i^{evf} + \psi_i^{evf} \rho_i^{ws} \overline{W}_i^{ws} \right), \quad (13)$$

where u_{ws} , u_{gm} , u_{sk} – specific internal energy of water-salt solution, gas mixture and soil skeleton, J/kg; ρ_{sk} – soil skeleton density, kg/m³; \vec{j}_q – heat flow through the soil, W/m²; h_i^{ws} – enthalpy of i -th component of water-salt solution, J/kg; h_l^{gm} – enthalpy of the l -th component of the gas mixture, J/kg.

Next, we substituted equations (6) - (9), (12) into equation (13) and derived the equation of changing rate of internal energy density:

$$\frac{\partial (\rho_{ws} u_{ws} + \rho_{gm} u_{gm} + \rho_{sk} u_{sk})}{\partial t} = -\nabla \cdot (\vec{j}_q) - P \nabla \cdot (n_{ws} \overline{W}_{ws}) - P \nabla \cdot (n_{gm} \overline{W}_{gm}) - \nabla \cdot (\rho_{ws} u_{ws} \overline{W}_{ws} + \rho_{gm} u_{gm} \overline{W}_{gm}) - \nabla \cdot \left(\sum_{i=1}^m h_i^{ws} \vec{j}_i^{ws} + \sum_{l=1}^k h_l^{gm} \vec{j}_l^{gm} \right) - \rho_{ws} \overline{W}_{ws} \cdot \vec{F}_{fr}^{ws} - \rho_{gm} \overline{W}_{gm} \cdot \vec{F}_{fr}^{gm} + \sum_{i=1}^m (\vec{j}_i^{ws} \cdot \vec{F}_i^{c,ws}) + \sum_{l=1}^k (\vec{j}_l^{gm} \cdot \vec{F}_l^{c,gm}) - \sum_{i=1}^m (\vec{j}_i^{ws} \cdot \vec{\nabla} \psi_i^{evf}). \quad (14)$$

Then we transformed the partial derivatives into convective for $u_{ws}, u_{gm}, n_{ws}\vec{W}_{ws}$ и $n_{gm}\vec{W}_{gm}$. Also we took into account the constant pore volume ($n_{ws} + n_{gm} = const$) and well-known correlation between enthalpy and internal energy ($du + PdV = dh - v dP$) and derived the equation of changing rate of internal energy density in enthalpy form:

$$\begin{aligned} \rho_{ws} \frac{dh_{ws}}{dt} + \rho_{gm} \frac{dh_{gm}}{dt} + \rho_{sk} \frac{dh_{sk}}{dt} - \frac{dP}{dt} = & -\nabla \cdot (\vec{J}_q) - \\ & -\nabla \cdot \left(\sum_{i=1}^m h_i^{ws} \vec{J}_i^{ws} + \sum_{l=1}^k h_l^{gm} \vec{J}_l^{gm} \right) - \\ & -\rho_{ws} \vec{W}_{ws} \cdot \vec{F}_{fr}^{ws} - \rho_{gm} \vec{W}_{gm} \cdot \vec{F}_{fr}^{gm} + \\ & + \sum_{i=1}^m (\vec{J}_i^{ws} \cdot \vec{F}_i^{c,ws}) + \sum_{l=1}^k (\vec{J}_l^{gm} \cdot \vec{F}_l^{c,gm}) - \\ & - \sum_{i=1}^m (\vec{J}_i^{ws} \cdot \vec{\nabla} \psi_i^{evf}), \end{aligned} \quad (15)$$

where h_{ws}, h_{gm}, h_{sk} – enthalpy of water-salt solution, gas mixture and soil skeleton, J/kg.

Next, we wrote the first law of thermodynamics in the enthalpy form for systems with variable concentration:

$$\begin{aligned} \rho_{ws} T \frac{ds_{ws}}{dt} = \rho_{ws} \frac{dh_{ws}}{dt} - n_{ws} \frac{dP}{dt} - \\ - \sum_{i=1}^m (G_i^{ws} + \psi_i^{ch}) \rho_{ws} \frac{d\omega_i}{dt}, \end{aligned} \quad (16)$$

$$\begin{aligned} \rho_{gm} T \frac{ds_{gm}}{dt} = \rho_{gm} \frac{dh_{gm}}{dt} - n_{gm} \frac{dP}{dt} - \\ - \sum_{l=1}^k G_l^{gm} \rho_{gm} \frac{d\omega_l}{dt}, \end{aligned} \quad (17)$$

$$\rho_{sk} T \frac{ds_{sk}}{dt} = \rho_{sk} \frac{dh_{sk}}{dt} - n_{sk} \frac{dP}{dt}, \quad (18)$$

where T – temperature, K; s_{ws}, s_{gm}, s_{sk} – entropy of water-salt solution, gas mixture and soil skeleton, J/kg; n_{sk} – volume fraction of mineral skeleton in soil, u.f.; G_i^{ws} – Gibbs free energy of i -th component of water-salt solution, J/kg; G_l^{gm} – Gibbs free energy of l -th component of gas mixture, J/kg; ω_l – mass concentration of l -th component of gas mixture, u.f.

Then we summed the equations (16) - (18), substituted into equation (15) and derived the entropy transfer equation:

$$\begin{aligned} \rho_{ws} \frac{ds_{ws}}{dt} + \rho_{gm} \frac{ds_{gm}}{dt} + \rho_{sk} \frac{ds_{sk}}{dt} = \\ = -\nabla \cdot \left(\frac{\vec{J}_q + \sum_{i=1}^m \vec{J}_i^{ws} (h_i^{ws} - G_i^{ws} - \psi_i^{ch}) + \sum_{l=1}^k \vec{J}_l^{gm} (h_l^{gm} - G_l^{gm})}{T} \right) - \\ - \frac{(\vec{J}_q^{ws} + \vec{J}_q^{gm} + \vec{J}_q^{sk})}{T^2} \nabla T + \\ + \sum_{i=1}^m \vec{J}_i^{ws} \left(\frac{\vec{F}_i^{c,ws} - (\vec{\nabla} (G_i^{ws} + \psi_i^{ch}))_T - \vec{v}_i \psi_i^{evf}}{T} \right) - \frac{\vec{J}_{ws} \cdot \vec{F}_{fr}^{ws}}{T} \\ + \sum_{l=1}^k \vec{J}_l^{gm} \left(\frac{\vec{F}_l^{c,gm} - (\vec{\nabla} G_l^{gm})_T}{T} \right) - \frac{\vec{J}_{gm} \cdot \vec{F}_{fr}^{gm}}{T}, \end{aligned} \quad (19)$$

where $\vec{J}_q^{ws}, \vec{J}_q^{gm}, \vec{J}_q^{sk}$ – heat flows through the water-salt solution, gas mixture and soil skeleton, which in summation is

heat flux through the soil \vec{J}_q , W/m²; $\vec{J}_{ws}, \vec{J}_{gm}$ – convective flow of water-salt solution and gas mixture, kg/(s·m²).

Analysis of equation (19) showed that it is a simple sum of three linearly independent equations, because there are three groups of independent summands. According to earlier assumptions about the interaction of the gas mixture and the water-salt solution only in the evaporation-condensation processes, which have zero tensor dimension, and the negligible rate of formation of the mineral skeleton of the ground from the matter in pore, we can consider the water-salt solution, the gas mixture and a skeleton of a ground separately.

The transport of matter in the gaseous form is negligible in soil with high water-salt solution and ice content [7]. Soil skeleton can transfer only energy according to earlier assumptions. All this allows us to neglect the transfer of matter in gaseous form. The transfer of the water-salt solution has the greatest interest in predicting of frost heaving. So we wrote (19) the form from which the volumetric source of entropy can be clearly separated:

$$\rho_{ws} \frac{ds_{ws}}{dt} = -\nabla \cdot \vec{J}_s + \sigma_s, \quad (20)$$

$$\vec{J}_s = \frac{\vec{J}_q^{ws}}{T} + \sum_{i=1}^m \vec{J}_i^{ws} \left(\frac{h_i^{ws} - G_i^{ws} - \psi_i^{ch}}{T} \right), \quad (21)$$

$$\begin{aligned} \sigma_s = -\vec{J}_q^{ws} \cdot \frac{\vec{\nabla} T}{T^2} - \frac{\vec{J}_{ws}}{T} \cdot \vec{F}_{fr}^{ws} - \\ - \sum_{i=1}^m \left(\vec{J}_i^{ws} \cdot \frac{(-\vec{F}_i^{c,ws} + v_i^p \vec{\nabla} P + \vec{\nabla} (\mu_i^c + \psi_i^{ch}))_T + \vec{v}_i \psi_i^{evf}}{T} \right), \end{aligned} \quad (22)$$

where v_i^p – specific volume of the i -th component in solution, as the ratio of volume to mass of the i -th component in solution, m³/kg; μ_i^c – decrease of Gibbs free energy of the i -th component in solution, due to the change of the concentration, J/kg

Equations (20) – (22) for the source of entropy is the basis for formulation the system of Onsager linear equations.

According to Onsager's theorem, source of entropy is determined by next expression:

$$\sigma_s = \sum_{k=1}^l \vec{J}_k \cdot \vec{X}_k. \quad (23)$$

Comparing (23) and (22) allowed us to write the flows and the thermodynamic driving forces. Specific friction force \vec{F}_{fr}^{ws} can be obtained from equation (5) for stationary flow:

$$\begin{aligned} \vec{J}_{ws} \rightarrow \vec{X}_{ws} = \vec{F}_{fr}^{ws} = v_{ws} \vec{\nabla} P + \\ + \sum_{i=1}^m (\omega_i \vec{v}_i \psi_i^{evf}) - \sum_{i=1}^m \omega_i \vec{F}_i^{c,ws}, \end{aligned} \quad (24)$$

$$\vec{J}_q^{ws} \rightarrow \vec{X}_q = \frac{\vec{\nabla} T}{T}, \quad (25)$$

$$\vec{J}_i^{ws} \rightarrow \vec{X}_i = \vec{\nabla} \psi_i^{evf} + v_i^p \vec{\nabla} P + \vec{\nabla} (\mu_i^c + \psi_i^{ch})_T - \vec{F}_i^{c,ws}, \quad (26)$$

where v_{ws} – specific volume of water-salt solution, m³/kg.

The key expressions (1), (4) allowed us to derive the following expression for the flow of the water-salt solution

$$\vec{J}_{ws} \rightarrow \vec{X}_{ws} = \vec{F}_{fr}^{ws} = v_{ws} \vec{\nabla} P + \sum_{i=1}^m (\omega_i \vec{\nabla} \psi_i) - \sum_{i=1}^m \omega_i \vec{F}_i^{c,ws}, \quad (27)$$

Each flow in nonequilibrium thermodynamics, unlike the classical theory of molecular transport, is caused by the simultaneous action of all thermodynamic driving forces multiplied by kinetic coefficients, The last is foundation of nonequilibrium thermodynamics and well-known like Onsager's theorem. We used Onsager's theorem for expressions (25) – (27), took into account equation for diffusion flows ($\sum_{i=1}^m \vec{J}_i^{ws} = 0$) and derived the systems of linear equations for thermodynamic driving forces and flows:

$$\begin{aligned} \vec{J}_{ws} &= L_{ws,ws} \vec{X}_{ws} + L_{ws,q} \vec{X}_q + \sum_{i=1}^{m-1} (L_{ws,i} (\vec{X}_i - \vec{X}_m)), \\ \vec{J}_q^{ws} &= L_{q,ws} \vec{X}_{ws} + L_{q,q} \vec{X}_q + \sum_{i=1}^{m-1} (L_{q,i} (\vec{X}_i - \vec{X}_m)), \\ \vec{J}_1^{ws} &= L_{1,ws} \vec{X}_{ws} + L_{1,q} \vec{X}_q + \sum_{i=1}^{m-1} (L_{1,i} (\vec{X}_i - \vec{X}_m)), \\ &\dots, \\ \vec{J}_j^{ws} &= L_{j,ws} \vec{X}_{ws} + L_{j,q} \vec{X}_q + \sum_{i=1}^{m-1} (L_{j,i} (\vec{X}_i - \vec{X}_m)), \\ &\dots, \\ \vec{J}_{m-1}^{ws} &= L_{m-1,ws} \vec{X}_{ws} + L_{m-1,q} \vec{X}_q + \\ &+ \sum_{i=1}^{m-1} (L_{m-1,i} (\vec{X}_i - \vec{X}_m)), \end{aligned} \quad (28)$$

where $L_{j,i}$ – kinetic transport coefficients.

The system of linear equations (28) describes the heat flux \vec{J}_q^{ws} , the convective flow \vec{J}_{ws} and the diffusion fluxes \vec{J}_i^{ws} in the m-component water-salt solution in the soil under the action of external mass forces, pressure gradients, temperature gradients, capillary-sorption and chemical potentials gradients of all components, that allow to predict frost heaving.

CONCLUSION

Authors used equation of the solution dynamics [5], changing rate of kinetic (6) – (7), potential (8)-(9), sorption (12), total (13) internal (14) energy and the first law of thermodynamics (16) – (18) to derive systems of the equations (28) of thermodynamic driving forces and flows using Onsager reciprocal relations.

Systems of equations (28) allow to predict frost heaving, associated with water inflow in freezing zone and next thermodynamic driving forces: external mass forces, pressure gradients, temperature gradients, all components capillary-sorption and chemical potentials gradients.

The application of equations (28) for a binary water-salt solution in soil will be described in more detail in the third part of this article.

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