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STRUCTURE OF THE SINGULAR TERMS IN THE FREE ENERGY CORRECTLY REPRODUCING THE NONASYMPTOTIC CORRECTIONS TO THE THERMODYNAMIC FUNCTIONS

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The method for selecting the structure of the singular terms in the expression for the free energy correctly reproducing the nonasymptotic components of the thermodynamic functions is examined.

The problem of describing a wide neighborhood of the critical point with the help of unified nonanalytical equations of state is solved in [1-13]. In these works, the starting thermodynamic functions — the internal energy $u(\rho, T)$ [1-6], the enthalpy i(p, T) [7, 8], the chemical potential $\mu(p, T)$ [9], the isochoric heat capacity $C_v(\rho, T)$ [10], and the Helmholtz free energy $F(\rho, T)$ [11-13] — are represented in the form of two terms: an irregular term satisfying a power law of the scaling theory (ST) and a regular function describing the characteristic features of the thermodynamic surface in the region of low densities and pressures.

The singular components of the equations of state [1-13] enable describing qualitatively correctly, i.e., in accordance with the requirements of the ST, the behavior of the thermody-namic surface only in an asymptotic neighborhood of the critical point: $|\Delta \rho| \leq 0.06$, $\tau \leq 0.01$. At the same time, according to [14, 15], in describing the properties of pure substances (in our case liquid-vapor systems) auxiliary nonanalytical terms, taking into account the next approximations of ST, must be included in the structure of the equations of state. These correction terms are calculated in [16] by the ε expansion method up to terms of order ε^2 . In accordance with the results of [16, 17], the behavior of a number of thermodynamic functions on characteristic lines of the thermodynamic surface is described in the critical region by the following power laws:

$$K_{T}(\rho_{\mathbf{c}}, T) = \Phi_{\mathbf{a}} \tau^{-\gamma} + \Phi_{\mathbf{i}} \tau^{-\gamma+\Delta}, \tag{1}$$

$$C_{v}(\rho_{c}, T) = \Gamma_{0}\tau^{-\alpha} + \Gamma_{1}\tau^{-\alpha+\Delta} + \Gamma_{2},$$
⁽²⁾

$$p(\rho, T_{c}) - p(\rho_{c}, T_{c}) = P_{\theta} \Delta \rho |\Delta \rho|^{\delta - 1} + P_{1} \Delta \rho |\Delta \rho|^{\delta - 1 + \frac{\Delta}{\beta}},$$
(3)

$$\mu(\rho, T_{\mathbf{c}}) - \mu(\rho_{\mathbf{c}}, T_{\mathbf{c}}) = R_0 \Delta \rho \left| \Delta \rho \right|^{\delta - 1} + R_1 \Delta \rho \left| \Delta \rho \right|^{\delta - 1 + \frac{\Delta}{\beta_1}}, \tag{4}$$

Here Φ_0 , Γ_0 , P_0 , R_0 are the constant coefficients in front of the asymptotic terms of the expressions (1)-(4), Φ_1 , Γ_1 , P_1 , R_1 are the constant coefficients in front of the nonasymptotic correction terms in the expressions (1)-(4).

The structure of the nonasymptotic terms has now been established only for the scale equations of state in parametric form:

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$$\Delta \mu \left(\rho, \ T \right) = a r^{\beta \delta} \theta \left(1 - \theta^2 \right) + e r^{\beta \delta + \Delta} \theta, \tag{5}$$

$$\tau = r \left(1 - b^2 \theta^2\right), \quad \Delta \rho = k r^b \theta, \tag{6}$$

where r is a variable characterizing the distance from the critical point, θ is an "angular" variable; and, $b^2 = (\gamma - 2\beta)/\gamma/(1-2\beta)$.

In constructing the wide-range nonanalytical equations of state, however, singular terms in the starting thermodynamic functions, written not in a parametric form but rather in terms of physical variables density-temperature [1-6, 10-13] or pressure-temperature [7-9] are used.

A method for constructing the singular components of the free energy in the density-temperature variables is proposed in [13]. But the region where the thermodynamic surface is described by the nonanalytical components of the free energy obtained in [13] is bounded by the asymptotic neighborhood of the critical point. A method for calculating the additional singular components in the starting thermodynamic functions, "responsible" for the nonasymptotic corrections to the thermodynamic quantities (see, for example, (1)-(4)), however, still does not exist. We shall show that this method can be based on the combined analysis of the asymptotes of the singular component of the free energy and power-law functionals with noninteger exponents.

We shall represent Helmholtz's free energy, which in the density-temperature variables is the characteristic function, in the form of a sum of two terms:

$$F(\rho, T) = \rho^{n_1} F_r(\rho, T) + F_r(\rho, T),$$
(7)

where $\rho^{n_1}F_1(\rho, T)$ and $F_p(\rho, T)$ are the irregular and regular components of the free energy, respectively.

It is desirable to represent the irregular component of the free energy $F_{i}(\rho, T)$ in the form of a sum of two functions:

$$F_{i}(\rho, T) = F_{i1}(\rho, T) + F_{i2}(\rho, T).$$
(8)

The function $F_{i_1}(\rho, T)$ entering into the formula (8) must reproduce the asymptotic terms of relations (1)-(4), while the function $F_{i_2}(\rho, T)$ must describe the nonasymptotic terms of the thermodynamic functions of these relations. The procedure for calculating $F_{i_1}(\rho, T)$ is examined in detail in [13].

To determine the structure of the nonasymptotic singular components of the free energy $F_{i_2}(\rho, T)$, we shall elucidate the nature of the behavior of its derivatives in the critical region. We substitute the expression (8) into the well-known thermodynamic equalities $p = \rho^2(\partial\rho F/\partial\rho)_T$, $K_T^{-1} = \rho(\partial p/\partial\rho)_T$, $\mu = (\partial\rho F/\partial\rho)_T$ and $\rho C_v = -T(\partial^2\rho F/\partial T^2)_{\rho}$. Then we compare the expressions found for the isothermal compressibility, isochoric heat capacity, pressure, and chemical potential with the scaling laws, describing the behavior of the substance on the characteristic lines of the thermodynamic surface $\Delta\rho = 0$, $\tau = 0$, $T = T_s(\rho)$ (see the expressions (1)-(4)). As a result we find that the function $F_{i_2}(\rho, T)$ correctly reproduces the nonasymptotic corrections to the thermodynamic functions (1)-(4) in the case when in the vicinity of the critical point its partial derivatives have the following asymptotes:

$$(\partial F_{i2}/\partial \rho)_{T,\tau=0} \sim \Delta \rho |\Delta \rho|^{\delta-1+\frac{\Delta}{\beta}}, \ (\partial^2 F_{i2}/\partial T^2)_{\rho,\tau=0} \sim |\Delta \rho|^{\frac{-\alpha+\Delta}{\beta}},$$
(9)

$$(\partial^2 F_{\mathbf{i}\,\mathbf{2}}/\partial\rho^2)_{T,\tau=0} \sim |\Delta\rho|^{\frac{\gamma+\Delta}{\beta}},\tag{10}$$

$$(\partial^2 F_{i2}/\partial T^2)_{\substack{\rho, \Delta \rho = 0 \\ x = -x_0}} \sim |\tau|^{-\alpha + \Delta}, \ (\partial^2 F_{i2}/\partial \rho^2)_{\substack{T, \Delta \rho = 0 \\ x = -x_0}} \sim |\tau|^{\gamma + \Delta}.$$
(11)

Here $x=\tau/|\Delta\rho|^{1/\beta}$ is a scaling variable; $x = -x_0$ is the equation of the curve of coexistence, valid in a small neighborhood of the critical point.

The characteristic behavior of the function $F_{i_2}(\rho, T)$, according to the dependences (9)-(11), is described by power laws with noninteger exponents. The solution of the problem posed must therefore be sought in the class of power-law functionals.

We represent the function $F_{i_2}(\rho, T)$ in the form of power-law functions, analogous to those studied in [13]:

$$F_{j2}(\rho, T) = Z_1(\rho, T)^{\xi_j},$$
(12)

$$F_{j_2}(\rho, T) = (Z_1(\rho, T) + Z_2(\rho, T)^{\xi_2})^{\xi_1},$$
(13)

$$F_{i2}(\rho, T) = \sum_{n=1}^{\infty} K_n Z_n(\rho, T)^{\xi_i} + \sum_{n=1}^{\infty} D_n Z_n(\rho, T)^{\xi_2},$$
(14)

where

$$Z_1(\rho, T) = \sum_{i,j=0} A_{ij} \tau^{\varphi_i} \Delta \rho^{\varepsilon_j}, \ Z_2(\rho, T) = \sum_{i,j=0} B_{ij} \tau^{\psi_i} \Delta \rho^{\eta_j}, \ldots$$

Here $\varphi_0 = \varepsilon_0 = \psi_0 = \eta_0 = 0$; $A_{00} = 0$; $\varphi_0 < \varphi_1 < \dots$; $\psi_0 < \psi_1 < \dots$; $\varepsilon_0 < \varepsilon_1 < \dots$; $\eta_0 < \eta_1 < \dots$; A_{ij} , B_{ij} , K_n , D_n are constant coefficients; and ξ_i , ψ_i , η_j , φ_i , ε_j are real exponents.

It is evident that for small values of τ and $\Delta\rho$ the characteristic features of the irregular function $F_{i_2}(\rho, T)$ and its derivatives are determined by the terms (12)-(14) with the lowest values of the exponents φ_i , ε_j , ψ_i and n_j . The problem posed thereby reduces to determining the quantities φ_1 , ε_1 , ψ_1 , η_1 , ξ_1 and ξ_2 in terms of the critical indices α , β , δ , and γ .

We shall show that it can be solved based on the proposed method for determining the structure of the nonasymptotic terms in the free energy $F_{i_2}(\rho, T)$. We shall first analyze the expression (13), from which follow immediately the values of the derivatives of the function $F_{i_2}(\rho, T)$ presented below:

$$\left(\frac{\partial^{F}_{12}}{\partial\rho}\right)_{T} = \xi_{1}(Z_{1}(\rho, T) + Z_{2}(\rho, T)^{\xi_{2}})^{\xi_{1}-1}Z_{3}(\rho, T),$$

$$\left(\frac{\partial^{2}F_{12}}{\partial\rho^{2}}\right)_{T} = \xi_{1}(\xi_{1}-1)(Z_{1}(\rho, T) + Z_{2}(\rho, T)^{\xi_{2}})^{\xi_{1}-1}Z_{3}(\rho, T)^{2} +$$

$$+ \xi_{1}(Z_{1}(\rho, T) + Z_{2}(\rho, T)^{\xi_{2}})^{\xi_{1}-1} \left[\sum_{i,j=0} A_{ij}\tau^{\psi_{i}}\Delta\rho^{e_{j}-2} \frac{\varepsilon_{j}(\varepsilon_{j}-1)}{\rho_{\kappa}^{2}} +$$

$$+ \xi_{2}\left(\sum_{i,j=0} B_{ij}\tau^{\psi_{i}}\Delta\rho^{\eta_{j}-2} \frac{\eta_{j}(\eta_{j}-1)}{\rho_{\kappa}^{2}}\right)Z_{2}(\rho, T)^{\xi_{2}-1} + \xi_{2}(\xi_{2}-1)\left(\sum_{i,j=0} B_{ij}\tau^{\psi_{i}}\Delta\rho^{\eta_{j}-1} \frac{\eta_{j}}{\rho_{\kappa}}\right)^{2}Z_{2}(\rho, T)^{\xi_{2}-2} \right],$$

$$+ \xi_{2}\left(\sum_{i,j=0} A_{ij}\tau^{\varphi_{i}-1}\Delta\rho^{e_{j}} \frac{\varphi_{i}}{T_{\kappa}} + \xi_{2}\left(\sum_{i,j=0} B_{ij}\tau^{\psi_{i}-1}\Delta\rho^{\eta_{j}} \frac{\psi_{i}}{T_{\kappa}}\right)Z_{2}(\rho, T)^{\xi_{j}-1} \right]^{2} +$$

$$+ \xi_{1}(Z_{1}(\rho, T) + Z_{2}(\rho, T)^{\xi_{2}})^{\xi_{1}-1} \left[\sum_{i,j=0} A_{ij}\tau^{\varphi_{i}-2}\Delta\rho^{e_{j}} \frac{\varphi_{i}(\varphi_{i}-1)}{T_{\kappa}^{2}} +$$

$$+ \xi_{2}\left(\sum_{i,j=0} B_{ij}\tau^{\psi_{i}-2}\Delta\rho^{\eta_{j}} \frac{\psi_{i}(\psi_{i}-1)}{T_{\kappa}^{2}}\right)Z_{2}(\rho, T)^{\xi_{j}-1} +$$

$$+ \xi_{2}(\xi_{2}-1)\left(\sum_{i,j=0} B_{ij}\tau^{\psi_{i}-1}\Delta\rho^{\eta_{j}} \frac{\psi_{i}}{T_{\kappa}}\right)^{2}Z_{2}(\rho, T)^{\xi_{j}-2} \right],$$

$$(17)$$

where

$$Z_{3}(\rho, T) \operatorname{sign} (\Delta \rho) \left[\sum_{i,j=0}^{\infty} A_{ij} \tau^{\varphi_{i}} \Delta \rho^{\varepsilon_{j-1}} \frac{\varepsilon_{j}}{\rho_{\kappa}} + \xi_{2} \left(\sum_{i,j=0}^{\infty} B_{ij} \tau^{\psi_{i}} \Delta \rho^{\eta_{j-1}} \frac{\eta_{j}}{\rho_{\kappa}} \right) Z_{2}(\rho, T)^{\xi_{2}-1} \right]$$

We shall analyze simultaneously the expressions for the partial derivatives of the function $F_{1_2}(\rho, T)$ (15)-(17) and the scaling relations (9)-(11). We substitute $\tau = 0$ into (15) and (16) and find that the corresponding relations (9) and (10) hold if the following equalities hold:



Fig. 1. Deviation of the scaling functions of the isochoric heat capacity $f_0(x)$ and chemical potential $h_0(x)$, calculated based on the scaling function of the free energy (29) of this work $(A_1 = -27.777, B_1 = -3.6985, C = -0.4482, x_1 = 0.5608, x_2 = 0.6433)$, from the corresponding scaling functions f(x) and h(x) of [17] for argon. The dependences of the deviations $\delta f = (f_0-f)/f_0$ (1) and $\delta h = (h_0-h)/h_0$ (2) are shown as a function of the scaling variable x.

$$\varepsilon_{1}\xi_{1} = \delta + 1 + \frac{\Delta}{\beta} = 2 + \frac{\gamma + \Delta}{\beta} .$$
(18)

It also follows from (16) that $\varepsilon_1 = 1$ or $\varepsilon_1 = 2$. In the opposite case, on the critical isochore $\Delta \rho = 0$ the derivative $(\partial^2 F_{12}/\partial \rho^2)_T$ either vanishes ($\varepsilon_1 < 2$) or diverges ($\varepsilon_1 \neq 2$ and $\varepsilon_1 \neq 1$), which contradicts (11).

On the other hand, if $A_{10} \neq 0$, then it follows from (17) that $\varphi_1 = 1$ or $\varphi_1 = 2$, since in the opposite case with $\tau = 0$ the derivatives $(\partial^2 F_{12}/\partial T^2)_{\rho}$ either diverges $(\varphi_1 < 2_{and} \varphi_1 \neq 1)$, or vanishes $(\varphi_1 > 2)$, which contradicts the corresponding expression (9)-(10). But then, acacording to the expression (11), the equality $\varphi_1\xi_1 = 2 - \alpha + \Delta$ must hold on the critical isochore (see (17)), which contradicts the conditions (18) found above for the exponents ε_1 , ξ_1 and the critical indices β , δ , Δ . The contradiction is resolved if in expression (13) and correspondingly in the formulas (15)-(17) the equalities $A_{10} = 0$, $A_{01} \neq 0$ or $A_{10} \neq 0$, $A_{01} = 0$ hold. Both indicated variants were studied. It turned out that if $A_{10} \neq 0$, $A_{01} = 0$, then the solution of the problem stated in the class of power-law functions (13) does not exist. In what follows we shall therefore assume that $A_{10} = 0$, $A_{01} \neq 0$.

In this case it follows from (17) that $\psi_1 = 1$ or $\psi_2 = 2$, since if $\psi_1 < 2$ and $\psi_2 \neq 1$, then the derivative $(\partial^2 F_{12}/\partial T^2)_{\rho}$ diverges on the critical isotherm and vanishes for $\psi_1 > 2$, which contradicts (9). Now we substitute into (17) $\Delta \rho = 0$, and comparing with the corresponding dependence (11) we obtain one more coupling condition for the exponents ψ_1 , ξ_1 , ξ_2 and the critical indices α , Δ :

$$\psi_1\xi_1\xi_2 = 2 - \alpha + \Delta. \tag{19}$$

On the other hand, in the limit $\Delta \rho \rightarrow 0$ it follows from the expressions (10) and (17) that if $\varepsilon_1 = 1$, then the equality

$$\psi_1 \xi_2 \left(\xi_1 - 1\right) = \gamma + \Delta \tag{20}$$

must hold. If however, $\varepsilon_1 = 2$, then

$$\psi_1 \xi_2 \left(\xi_1 - 2 \right) = \gamma + \Delta. \tag{21}$$

In order to describe correctly the behavior of the nonasymptotic term of the isochoric heat capacity on the critical isotherm (see (9), (17)), it is sufficient to demand that in the case $\psi_1 = 1$ the equality

$$\eta_1(\xi_1\xi_2 - 1) = (-\alpha + \Delta)/\beta,$$
(22)

hold, while for $\psi_1 = 2$

$$\eta_1(\xi_1\xi_2-2) = (-\alpha + \Delta)/\beta.$$
(23)

We now substitute the dependence $\tau = -x_0 |\Delta \rho|^{1/\beta}$ into (16) and (17), and we find that in order to satisfy the relations (11) on the coexistence curve $x = -x_0$, it is sufficient to require that the following equalities hold:

$$\varepsilon_1 \xi_1 = 2 + (\gamma + \Delta)/\beta, \quad \psi_1 \xi_1 \xi_2 = 2 - \alpha + \Delta. \tag{24}$$

Using Griffith's equalities $2 - \alpha = \beta \delta + \beta$, $\gamma = \beta \delta - \beta$, we obtain from the relations (18)-(24) a system of equations enabling the calculation of the values of the exponents ε_1 , ψ_1 , η_1 , ξ_2 , ξ_1 in terms of the critical indices:

$$\eta_1 \xi_2 = \varepsilon_1, \ \varepsilon_1 \xi_1 = 1 + \delta + \Delta/\beta, \ \psi_1 \xi_1 \xi_2 = 2 - \alpha + \Delta, \tag{25}$$

where the parameters ε_1 and ψ_1 assume the values 1 or 2.

Thus based on the combined analysis of the derivatives of the function $F_{12}(\rho, T)$ (15)-(17) and the scaling relations (9)-(11) in the class of power-law functions (13) the structure of the singular component of the free energy $F_{H2}(\rho, T)$, satisfying the requirements (1)-(4) has been determined:

$$F_{i2}(\rho, T) = [A_{01}\Delta\rho^{\epsilon_1} + (B_{01}\tau^{\psi_1} + B_{10} | \Delta\rho|^{\eta_1})^{\xi_2}]^{\xi_1},$$
(26)

where the components ε_1 , ψ_1 , η_1 , ξ_1 and ξ_2 are determined from the system of equations (25).

An analogous method for choosing the structure of the nonasymptotic terms of the thermodynamic functions was used in the analysis of the power-law functions (10) and (14). It turned out that in the class of power-law functions (12) the problem posed does not have a solution. In the class of functionals (14) the following structural forms of the function $F_{i_2}(\rho, T)$, satisfying all requirements (9)-(11) and, therefore, the scaling relations (1)-(4), were found:

$$F_{12}(\rho, T) = \sum_{n=1}^{\infty} K_n (A_{0n} \tau^{\varphi_1} + A_{n0} |\Delta \rho|^{\omega_1})^{\xi_1} + \sum_{n=1}^{\infty} D_n (B_{0n} \tau^{\psi_1} + B_{n0} |\Delta \rho|^{\eta_1})^{\xi_2},$$
(27)

where A_{0n} , A_{n0} , B_{0n} , $B_{n0} > 0$; φ_1 , ω_1 , ξ_1 , ψ_1 , η_1 , ξ_2 are real numbers satisfying the coupling conditions:

$$\begin{aligned} \phi_{1}\xi_{1} &= 2 - \alpha + \Delta, \ \omega_{1}\xi_{1} &= 1 + \delta + \Delta/\beta, \ \phi_{1} &= 1 \text{ or } 2, \\ \eta_{1} &= \psi_{1}/\beta, \ \xi_{2}\psi_{1} &= \beta \left(\delta - 1\right) + \Delta, \ \psi_{1} &= 1 \text{ or } 2. \end{aligned}$$
(28)

The nonasymptotic terms of the free energy (26) and (27), obtained in this work, together with the asymptotic terms $F_{11}(\rho, T)$ calculated in [13], enable describing in the physical variables density-temperature the scaling properties of pure substances in a wide neighborhood of the critical point: $0.7\rho_c < \rho < 1.3\rho_c$ in the density and from the curve of coexistence to $1.3T_c$ in the temperature [17].

We note that all solutions found (see expressions (26) and (27)) can be divided into two groups. The first group includes the singular terms of the free energy (26) and (27) in which $\varepsilon_1 = \varphi_1 = \psi_1 = 1$. In this case the isotherms are discontinuous in the two-phase region on the lines $\overline{A_{01}\tau} + A_{10} |\Delta \rho|^{1/\beta} = 0$ or $\overline{B_{01}\tau} + \overline{B_{10}} |\Delta \rho|^{1/\beta} = 0$, which can be interpreted as the "pseudo-spinodal" curves [18]. In the case $\varepsilon_1 = \varphi_1 = \psi_1 = 2$ we obtain the second group of singular terms in the free energy. The isotherms calculated on the basis of the indicated group have the form of the van der Waals equation. In this sense the second group of singular terms of the free energy reproduces the thermodynamic surface just as the scaling equation of state in parametric form [19, 20], which gives rise to the appearance of only one singular point — the critical point — on the thermodynamic surface.

A comparative analysis of the singular terms obtained in the free energy (27) as well as the scaling functions of the isochoric heat capacity and chemical potential, calculated on their basis, with the corresponding functions obtained from the equation of state (5) showed that the dependence

$$F_{n2}(\rho, T) = |\Delta\rho|^{\delta+1+\frac{\Delta}{\beta}} [A_1((x+x_1)^{2-\alpha+\Delta} + \varepsilon (x+x_2)^{2-\alpha+\Delta}) + B_1(x+x_1)^{\gamma+\Delta} + C],$$
(29)

where $\varepsilon = -x_1/x_2$ reproduces most fully the nonasymptotic terms of the thermodyanmic functions.

For example, for argon in a wide neighborhood of the critical point the disagreement between the scaling functions of the isochoric heat capacity and chemical potential, calculated on the basis of expression (29), and the scaling functions of the parametric equation of state (5) (see, for example, [17])

$$h(x) = e\theta(k|\theta|)^{-\delta-\Delta}, \quad f(x) = \frac{ek}{2b^2}(\gamma+\Delta)\frac{(k|\theta|)^{\frac{\alpha-\Delta}{\beta}}}{1-(1-2\beta)b^2\theta^2}$$
(30)

does not exceed 9.8 and 6.8%, respectively (see Fig. 1).

NOTATION

u, internal energy; i, enthalpy; μ , chemical potential; C_v , isochoric heat capacity; F, free energy; ρ , density; T, absolute temperature; p, pressure; K_T, isothermal compressibility; ρ_c and T_c , critical parameters; f(x) and h(x), scaling functions of the isochoric heat capacity and chemical potential; $x=\tau/|\Delta\rho|^{1/\beta}$, a scaling variable; α , e, and k, constants characterizing the singularities of the given substance; $x = -x_0$, equation of the coexistence curve; α , β , σ , γ , Δ , critical indices; r and ϑ , "polar" coordinates; and $\Delta\rho = (\rho - \rho_c)/\rho_c$; $\tau = (T - T_c)/T_c$.

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HEAT EMISSION ACCOMPANYING THAWING OF A VERTICAL ICE SURFACE

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A dependence is proposed for determining the heat-transfer coefficient at the boundary of an ice massif and a water film running down the ice in the presence of thawing.

Heat transfer from air to an ice massif during the summer occurs through the liquid film which is formed and runs down the surface of the ice. This films plays the role of a thermal insulator for the ice massif. It runs down under the action of gravity, and its flow has a wave character [1, 2]. The thickness of the film varies over the height, so that the coefficient of heat transfer must be regarded as variable, which causes nonuniform thawing of the ice massif: thawing will be greater at the top than at the bottom.

Thawing of vertical surfaces was studied previously in [3, 4], but the factor responsible for this process was assumed to be film condensation. This enabled assuming that the boundary temperature at the outer surface of the thawing medium is equal to the condensation temperature. The solutions are presented in a form such that a computer is required to obtain numerical results; in addition, the deviation of the results from the exact solution under some conditions reaches 20% [4].

Figure 1 shows the diagram for the calculation of the magnitude of the thawing of a vertical wall of an ice massif.

The heat flow from the air to the liquid film formed is determined by the expression

$$q_{air} = \alpha_{air} (T_a - T_s). \tag{1}$$

This heat is transferred through the liquid film to the ice massif, with the exception of a small fraction expended on increasing the heat content of the liquid volume.

The heat flow through the liquid film in the section x is equal to

$$q = \alpha_x \left(T_s - T_{\rm m} \right). \tag{2}$$

This quantity can be expressed differently for a laminar fluid motion:

$$q = \frac{\lambda}{\delta_x} (T_s - T_m). \tag{3}$$

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