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INVESTIGATION OF THE DYNAMIC LOADING OF ICE

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The results of experiments [1, 2] show that the kinetics of phase transitions of some forms of H_2) into others play an important role in the formation of the complex wave patterns that arises when ice is subjected to an explosion or a shock. Thus, according to the data presented in [1], in the 150-200 MPa pressure range ice I begins to melt, at pressures from 200 MPa to 500 MPa a mixture of ice I and water is formed, and at pressures from 600 MPa to 1700 MPa the final phase is ice VI (the experiment was carried out on a specimen of ice I at a temperature $T = (263 \pm 2)$ K). If we take into account the fact that under thermodynamic equilibrium conditions the regions in which ice I can exist in the 240-273 K temperature range is limited to pressures of the order of 200 MPa, the beginning of this phase of ice up to a pressure of 500 MPa confirms that phase transitions in ice are of a nonequilibrium character.

The general principles for describing condensed media with phase transitions, based on the laws of the thermodynamics of irreversible processes, on certain models of the kinetics of phase transitions are presented in [3]. An approach to describing two-phase media with a phase transition, proposed in [4], was generalized in [5] to the case of N coexisting transformable phases and was used to investigate the shock loading of bismuth. A review of the results of theoretical and experimental investigations on phase transitions for the case of shock-wave loading of materials can be found in [6, 7].

In this paper we carry out a theoretical investigation of the loading of ice taking the kinetics of the phase transitions into account. The thermal equations of state and the thermodynamic properties of ice I, III, V, and VI and water, established previously in [8, 9], are used to describe the rapid loading of ice and the dynamics of the phase transitions. The theoretical results obtained are compared with experiment.

1. p-T-Diagram of H_2O and Model of a Multiphase Medium. To investigate the loading of ice, taking kinetic effects into account, we will take the temperature T and the pressure p as the independent variables. In Fig. 1 we show a p-T phase diagram of H_2O in the temperature range $240 \le T \le 300$ K and pressure range $0 \le p \le 10^3$ MPa. We will denote the set of (p, T) points corresponding to Fig. 1 by Ω. The results of a detailed study of the thermodynamic properties of ice and water in these pressure and temperature ranges are given in [8, 9]; the thermal equations of state of ice I, III, V and VI and liquid water were obtained, and their thermodynamic properties were also established. These results are used to investigate the effect of the kinetics on the loading of ice.

Following [9], we will denote quantities relating to ice I, III, V, VI and water by the symbols 1, 3, 5, 6, and w respectively. We will denote the set of symbols by Ψ, we will denote the region i ($i \in \Psi$), in which a thermodynamically stable phase exists by Ω_i, and we will denote the lines of phase transitions by a pair of indices written in braces: $\{ij\}$. As can be seen from Fig. 1, the p-T-diagram of H_2O is extremely complex: in comparatively narrow ranges of variation of the temperature and pressure the set Ω includes at least five phases and seven phase-transition lines. In [9] the equations $p = p_{ij}(T)$, used for an analytic description of the lines $\{ij\}$, are given in [9].

When investigating the dynamic loading of ice we will start from the following assumptions [3, 5, 7]: 1) the shear stresses which occur when ice is deformed are negligibly small, so that the pressure p is the only important characteristic stress tensor (the basis for this assumption, as it applies to ice, is discussed in [8, 9]), 2) the mixed H_2O phase, which is formed when ice is loaded, is macroscopically uniform, but consists microscopically of small inclusions of the pure phases, and we will neglect possible surface effects, 3) all the inclusions of the pure phases are in local thermodynamic equilibrium, although the mixture as a whole may be in a nonequilibrium state, 4) the temperature and pressure are the same for all the phases making up the mixture, and 5) the loading is adiabatic.

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TABLE 1

Value of the subscript i	$f_{i1}(T)$	$f_{i3}(T)$	$f_{i5}(T)$	$f_{i6}(T)$	$f_{iw}(T)$
1		$p_{13}(T)$	$p_{13}(T)$	$p_{13}(T)$	$p_{1w}(T)$
3	$p_{13}(T)$		$p_{35}(T)$	$p_{35}(T)$	$p_{3w}(T)$
5	$p_{35}(T)$	$p_{35}(T)$		$p_{56}(T)$	$p_{5w}(T)$
6	$p_{56}(T)$	$p_{56}(T)$	$p_{56}(T)$		$p_{6w}(T)$
w	$p_{1w}(T)$	$p_{3w}(T)$	$p_{5w}(T)$	$p_{6w}(T)$	

TABLE 2

Value of the subscript i	d_{i1}	d_{i3}	d_{i5}	d_{i6}	d_{iw}
1		−1	−1.	−1	−1
3	1		−1	−1	1
5	1	1		−1	1
6	1	1	1		1
w	1	−1	−1	−1	

Starting from assumptions 1-4, we will introduce the specific internal energy and the specific volume of the mixture of phases by the formulas

$$E(p,T) = \sum_{i\in\Psi} x_i E_i(p,T); \tag{1.1}$$

$$V(p,T) = \sum_{i\in\Psi} x_i V_i(p,T). \tag{1.2}$$

Here $E_i(p, T)$ and $V_i(p,T)$ are the specific internal energy and the specific volume of the i-th pure phase, respectively, and x_i is the mass fraction of phase i in the mixture. The summation in (1.1) and (1.2) is carried out over all the subscripts i belonging to the set of indices Ψ. The following obvious relations hold for x_i:

$$\sum_{i\in\Psi} x_i = 1, \qquad 0 \leqslant x_i \leqslant 1 \qquad (i \in \Psi).$$

When the ice is loaded, when there are phase transitions, the quantities $x_i (i \in \Psi)$ vary with time. To complete the formulation of the model we need to specify the kinetic relations describing the rate of change of x_i.

2. Description of the Kinetics of the Phase Transition in Ice. We will denote the rate of change of x_i when phase i changes into phase j (i, j $\in \Psi$) by α_{ij}. Assuming the quantities α_{ij} to be non-negative for any paris of indices, we can write

$$\frac{dx_i}{dt} = \sum_{\substack{j\in\Psi \\ j\neq i}} (\alpha_{ji} - \alpha_{ij}). \tag{2.1}$$

In each difference $\alpha_{ji} - \alpha_{ij}$ in the sum (2.1) only one of the terms can be nonzero, while the second must necessarily be zero.

Different models have been used previously to specify the quantities α_{ij}. In the simplest case of two-phase mixtures [6] it is assumed that α_{12} is proportional to the difference between x_1 and its equilibrium value. It was assumed in [5] that α_{ij} are proportional to $G_i - G_j$, where G is the Gibbs function of the corresponding phase. If we assume that only small deviations from the equilibrium states occur in a phase transition, the difference $G_i - G_j$ can be expanded in powers of $p - p_{ij}(T)$ [3] ($p = p_{ij}(T)$ is the equation of the line {ij} retaining only linear terms, and then α_{ij} are proportional to the differences $p - p_{ij}(T)$.

A generalization of the relation $\alpha_{ij} \sim p - p_{ij}(T)$ to the case of comparatively large deviations of the point (p, T), corresponding to the mixed phase, from the phase-equilibrium line, was proposed in [3] for a two-phase mixture. In the present paper we will use th following law of variation of α_{ij}, which generalizes the relation proposed in [3] to the case of N coexisting phases:

$$\alpha_{ij} = \begin{cases} x_i A_{ij}\{1 - \exp[d_{ij}(p - f_{ij}(T))\Delta_{ij}^{-1}]\}, \\ \qquad \text{if} \quad x_i > 0 \text{ and } (p,T) \in \Omega_j, \\ 0, \quad \text{if} \quad x_i = 0 \quad \text{or} \quad (p,T) \notin \Omega_j. \end{cases} \tag{2.2}$$

Here A_{ij} and Δ_{ij} are constants, $f_{ij}(T)$ are functions of the temperature, and $d_{ij} = \pm 1$. The expressions for the functions $f_{ij}(T)$, and also the values of d_{ij} for all pairs of indices i, j $\in \Psi$ ($i \neq j$) used in (2.2), are given in Tables 1 and 2.

We will discuss the choice of the functions $f_{ij}(T)$ in (2.2). If the regions Ω_i and Ω_j in which the phases i and j exist in a thermodynamically stable state have a common boundary, we can choose the equation of the corresponding phase-transition line as the function $f_{ij}(T)$. It may turn out, however, that at the point (p,T) which is in the region in which the phase j is stable, the mixture contains phase i, the region Ω_i of which has no common boundary with Ω_j. For example, according to the data given in [1], ice I is present in a mixture of phases up to pressures of 500 MPa, which may correspond to Ω_5 – the region in which ice V is stable. In such cases we will choose the following model for ice I in this paper: the rate of possible transition of ice I into ice V or ice VI is greater the more the pressure p exceeds the maximum possible value of the pressure for the given temperature T in region Ω, i.e., the value of $p_{13}(T)$. Consequently, we will use $p_{13}(T)$ as the functions $f_{15}(T)$ and $f_{16}(T)$. The choice of the functions $f_{ij}(T)$ for other pairs of indices i, j $\in \Psi$ in a similar situation is shown in Table 1.

The parameters A_{ij} in (2.2) represent the maximum possible rate of phase transitions, while Δ_{ij} are the characteristic values of the differences $|p - f_{ij}(T)|$ [3]. When choosing Δ_{ij} we will take into account in this paper the extent of the zones $\Omega_i (i \in \Psi)$ on the p-T-diagram, and also the data given in [1] on the phase composition of the multiphase mixture formed when ice is loaded.

The choice of the values of A_{ij} was governed by the presence of a characteristic time, which in the experiments carried out in [1] amounted to $L/D = 2.5 \cdot 10^{-5}$ sec (where L is the thickness of the ice specimen (of the order of 10^{-1} m) and D is the velocity of propagation of shockwave (about $4 \cdot 10^3$ m/sec)). It was also assumed, as in [5], that the transitions between the solid and liquid phases are slower processes than the transitions from one solid phase to another. The chosen values of A_{ij} and Δ_{ij} used in the calculations are given in the appendix. Note that, at the present time, there is no quantitative physical theory which enables these quantities to be calculated with the necessary accuracy for specific materials. The values of A_{ij} and Δ_{ij} given in the appendix must be regarded as parameters of the chosen model, which may be refined as the microscopic kinetic theory of phase transitions develop and as new experimental data are acquired.

3. Calculation of the Dynamic Loading of Ice. A calculation of the equilibrium melting of ice I, III, V, and VI was made in [8, 9] for quasistatic adiabatic loading along the melting curves {1w}, {3w}, {5w} and {6w} respectively. From the kinetic point of view the rate of such loading is so small that the phase transitions occur "instantaneously," so that, at each instant of time, the two-phase mixture is in a state of thermodynamic equilibrium.

To study the effect of kinetic phase transitions on the dynamic loading of ice we will consider the following problem. Suppose unit mass of ice, initially at a temperature T_0 and pressure p_0, is subjected to adiabatic dynamic loading, described by the relation $p = p(T)$, where t is the time. To determine the state of the ice when $t > 0$ we must integrate the following system of equations:

$$\frac{dE}{dt} + p\frac{dV}{dt} = 0; \tag{3.1}$$

$$\frac{dx_i}{dt} = F_i(p,T) \quad (i = 1, 3, 5, 6, w), \tag{3.2}$$

$$E(p,T) = \sum_{i\in\Psi} x_i E_i(p,T), \quad V(p,T) = \sum_{i\in\Psi} x_i V_i(p,T), \quad p = p(t).$$

The functions $F_i(p, T)$ are given by relations (2.1) and (2.2). Using the thermodynamic equations

$$-\frac{1}{V_i}\left(\frac{\partial V_i}{\partial p}\right)_T = \beta_{Ti}, \quad \frac{1}{V_i}\left(\frac{\partial V_i}{\partial T}\right)_p = \alpha_{Ti},$$

$$H_i(p,T) = E_i + pV_i, \quad \left(\frac{\partial E_i}{\partial p}\right)_T = V_i(p\beta_{Ti} - T\alpha_{Ti})$$

(β_{Ti} is the coefficient of isothermal compressibility, α_{Ti} is the coefficient of volume expansion, and H_i is the enthalpy of phase i), and transforming Eqs. (3.1) and (3.2), we arrive at the Cauchy problem of determining the functions T(t) and $x_i(t)$ which satisfy the following system of ordinary differential equations when t > 0:

$$\begin{gathered}\frac{dT}{dt} = \Big[\sum_{i\in\Psi}(-H_iF_i + \dot{p}(t)Tx_i\alpha_{Ti}V_i)\Big]\Big\{\sum_{i\in\Psi}x_i\Big[\Big(\frac{\partial E_i}{\partial T}\Big)_p + p\alpha_{Ti}V_i\Big]\Big\}^{-1}, \\ \frac{dx_i}{dt} = F_i(p,T) \qquad (i = 1, 3, 5, 6, w), \qquad p = p(t),\end{gathered} \tag{3.3}$$

and also the initial conditions when t = 0:

$$T = T_0, \quad x_1 = 1, \quad x_3 = 0, \quad x_5 = 0, \quad x_6 = 0, \quad x_w = 0. \tag{3.4}$$

Here we have denoted the derivatives dp/dt by $\dot{p}$. The relation p(t) is assumed given. In the problem considered we will assume

$$p(t) = p_*t/t_* \qquad (0 \leqslant t \leqslant t_*). \tag{3.5}$$

By varying the parameters p_* and t_* we can investigate the effect of the amplitude and rate of loading on the phase state of unit mass of ice.

System (3.3), with initial conditions (3.4), was integrated numerically by the Runge–Kutta method. For the functions E_i, H_i, α_{Ti}, V_i ($i \in \Psi$) we used the relations established earlier in [8, 9]. The initial temperature T_0 was chosen to be 263 K, while the pressure in (3.5) $p_* = 10^3$ MPa. The calculations were carried out for two values of the loading time (formula (3.5)): $t_* = 3\cdot10^{-6}$ sec and $3\cdot10^{-5}$ sec. Moreover, to take into account the effect of the initial temperature on the rapid loading of ice we integrated (3.3) and (3.4) at $T_0 = 253$ K and $t_* = 3\cdot10^{-6}$ sec. When solving (3.3) and (3.4) at each step in time we calculated the functions T(x) and $x_i(t)$ and then, using (1.2), we calculated the values of the specific volume of the mixture V. This enabled us to draw p – T and p – V diagrams of the dynamic loading of ice. The results of the calculations are shown in Figs. 1-3.

In Fig. 1 we have plotted lines of equilibrium phase transitions {ij}, separating the regions Ω_i ($i \in \Psi$) where the ice phases are thermodynamically stable. Here 1 is the trajectory of the states of the multiphase mixture corresponding to T_0 = 263 K and $t_* = 3\cdot10^{-6}$ sec, while 2 is the similar trajectory for T_0 = 263 K and $t_* = 3\cdot10^{-5}$ sec, while the dashed curve is for T_0 = 253 K and $t_* = 3\cdot10^{-6}$ sec. It can be seen that a change in the time of application of the load or of the initial temperature of the ice considerably changes the trajectory of the states of the multiphase mixture on the p – T diagram.

In Fig. 2 we show a p-V diagram, where the small circles, triangles, rhombuses and crosses represent the data of static experiments [10], bounding the regions in which two-phase mixtures of water and ice I, III, V, and VI exist in equilibrium, while the squares represent the results obtained in [1] on the shock loading of a specimen of ice at T_0 = (263 ± 2) K. It can be seen that the data on the dynamic loading differ considerably from the results of the static experiments. The calculated curve 1, as also in Fig. 1, corresponds to T_0 = 263 K and $t_* = 3\cdot10^{-6}$ sec, curve 2 corresponds to T_0 = 263 K and $t_* = 3\cdot10^{-5}$, while the dashed curve corresponds to T_0 = 253 K and $t_* = 3\cdot10^{-6}$ sec. As follows from Fig. 2, the rapid loading of ice has an extremely nonequilibrium character, while curve 1 corresponds to the experimental data on dynamic loading.

In Fig. 3 we show the change with time of the mass fractions of the phases of ice in a multiphase mixture for loading at T_0 =263 K and $t_* = 3\cdot10^{-6}$ sec. the numbers 1, 5, and 6 and the letter w in Fig. 3 relate to x_1, x_5, x_6, and x_7. The dynamics of the quantities x_i are determined by the duration of the loading t and the parameters A_{ij} and Δ_{ij} in (2.2).

Hence, in this paper, using the thermal equations of state derived in [8, 9] and the thermodynamic functions of ice I, III, V, VI and water in the 240-300 K temperature range and the 0-10^3 MPa pressure range we have constructed a model of the loading of ice, taking into account the kinetics of the phase transitions. Numerical calculations have been carried out and the p-V and p-T diagrams of state of a multiphase mixture have been constructed for different values of the loading time and for different initial temperatures. The curve on the p-V diagram for T_0 = 263 K and $t_* = 3\cdot10^{-6}$ sec agrees with experimental data [10] on the shock loading of ice. It has been established that a change in the duration of the load or of the initial temperature in this model has a considerable effect on the phase state of the mixture.

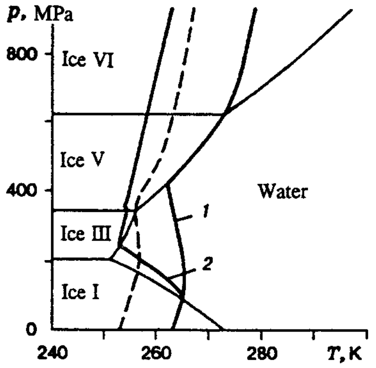

Fig. 1

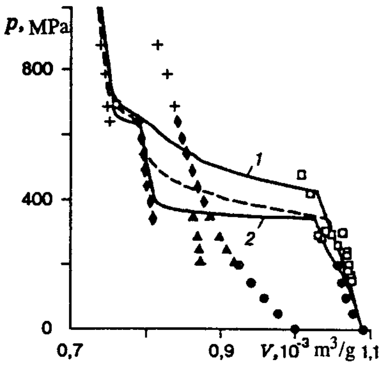

Fig. 2

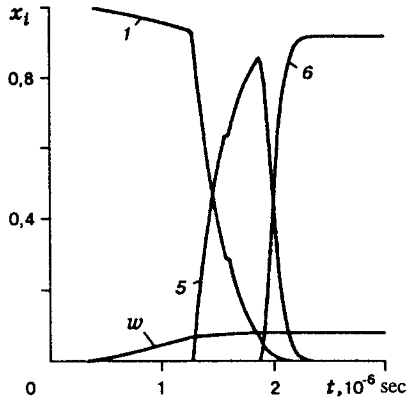

Fig. 3

The results obtained can provide a basis for mathematical modelling of the propagation of compression waves in ice, taking the kinetics of phase transitions into account

4. Appendix. 1. The numerical values of A_{ij}, $\sec^{-1}$ are as follows:

$$A_{13} = 1\cdot 10^5,\quad A_{15} = 3\cdot 10^7,\quad A_{16} = 3\cdot 10^7,\quad A_{1w} = 1\cdot 10^5,$$
$$A_{35} = 1\cdot 10^7,\quad A_{36} = 1\cdot 10^7,\quad A_{3w} = 1\cdot 10^5,\quad A_{56} = 3\cdot 10^7,$$
$$A_{5w} = 2\cdot 10^5,\quad A_{6w} = 2\cdot 10^5,\quad A_{w5} = 1\cdot 10^4,\quad A_{w6} = 1\cdot 10^4.$$

2. The numerical values of Δ_{ij}, MPa are as follows:

$$\Delta_{13} = 1\cdot 10^3,\quad \Delta_{15} = 1\cdot 10^3,\quad \Delta_{16} = 1\cdot 10^3,\quad \Delta_{1w} = 1\cdot 10^2,$$
$$\Delta_{35} = 5\cdot 10^2,\quad \Delta_{36} = 5\cdot 10^2,\quad \Delta_{3w} = 5\cdot 10^2,\quad \Delta_{56} = 1\cdot 10^2,$$
$$\Delta_{5w} = 5\cdot 10^1,\quad \Delta_{6w} = 5\cdot 10^1,\quad \Delta_{w5} = 1\cdot 10^2,\quad \Delta_{w6} = 1\cdot 10^2.$$

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