EVOLUTION OF A SYSTEM OF NUCLEI GROWING IN THE DIFFUSION REGIME WITH FLUCTUATING RATES

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Many problems related to the study of kinetics of introducing a new phase into a metastable master medium are solved on the basis of concepts of formation and subsequent evolution of the system of nuclei of the new phase. As examples one can quote studies of processes of massive crystallization [1-9], gas condensation [10-12], and phase stratification of colloids [13, 14]. All these problems are mathematically formulated identically with the use of a size distribution density of new phase formation. For a long time the variations in the distribution function were described by means of the continuity equation in the size space [1-3, 6, 8-14] with corresponding boundary conditions, reflecting the appearance of supercritical nuclei, and including the energy or material balance in the system. For homogeneous phase formation, however, a similar approach provides a discontinuous solution for the distribution function, while at the same time the experimental investigations indicate a continuous spectrum distributed over sizes [15-17]. These results lead to the necessity of including fluctuations in the rate of growth of a single isolated size. The problems generated have been investigated quite in detail for the kinetic regime of rate of formation for various nucleation types [4, 5, 7].

The formation phase of the basic mass of the new phase is treated below for the diffusion regime, for which the growth in isolated extractions is limited by the diffusion material supply from the parent metastable medium to the surface of separation. The shape of the new phase is assumed to be spherical, while for the medium it is concentration-supersaturated.

In treating fluctuations in the rate of growth of the distribution function of separate sizes f(t, r) varies according to the Fokker–Planck evolution equation

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial r}\left(\frac{dr}{dt}f\right)=\frac{\partial^2}{\partial r^2}(Bf) \tag{1}$$

(B is the effective diffusion coefficient along the radius axis). The distribution function is normalized by the formation number of the new phase per unit volume N(t).

The initial and boundary conditions for Eq. (1) are

$$f(0,r)=0,\quad r>r_*,$$
$$\left[-B\frac{\partial f}{\partial r}+\frac{dr}{dt}f\right]_{r=r_*}=J(\Delta\eta),\quad t>0, \tag{2}$$

where r_* is the critical nucleus radius, $\Delta\eta$ is the absolute supersaturation of the medium (the difference between the medium density and the equilibrium density), and J is the frequency of formation of supercritical nuclei per unit volume, in $\text{cm}^{-3}\cdot\text{sec}^{-1}$.

It is natural to expect that the most substantial effect of fluctuations in the growth rate occurs for nearly critical nuclei ($r \approx r_*$), whose formation and rate are determined by the fluctuation process of overcoming the critical potential barrier. These effects are investigated within the initial stage of phase transition – the nucleation stage [1]. The subsequent formation phase of fundamental mass of the new phase considered here is characterized by a high generation rate of supercritical nuclei, accompanied by a decrease in the extent of metastabilization. In this phase there are no recondensation processes, since the characteristic size of the isolated new phase is much larger than the critical radius, and the number of nearly critical nuclei is negligibly small. Therefore, similarly to [2-9, 11-14], in the following it is permissible to put $r_* = 0$. Finally, the given assumption involves some error in the shape of the distribution function in the region $r \approx r_*$, but is inconsequential in the region of interest $r \gg r_*$.

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The rate of growth dr/dt in the diffusion regime is

$$\frac{dr}{dt} = \frac{\psi(\Delta\eta)}{r}, \quad \psi(\Delta\eta) = D\Delta\eta(t)/\rho. \tag{3}$$

Here D is the material diffusion coefficient in the parent medium, in cm^2/sec, and ρ is the new phase density.

During the phase formation process one must satisfy the material balance condition of the material:

$$\Delta\eta(t) = \Delta\eta(0) - \frac{4}{3}\pi\rho\int_0^\infty r^3 f(t, r)\,dr \tag{4}$$

[$\Delta\eta(0)$ is the initial supersaturation].

Substantial information concerning the dependence of the coefficient B on the process parameters is quite incomplete, and there exist several opinions concerning this problem. According to several studies [15-17], the diffusion coefficient in the size space is directly proportional to the function $\psi(\Delta\eta)$ in (3), having a quite clear physical justification. Therefore, to analyze the effect of fluctuations in the growth rate on the kinetics of phase formation we use the expression $B = B_0\psi$, i.e., we neglect the possible dependence of B on the radius r. For $B_0 \to 0$ one obtains the problem in the absence of fluctuations.

Thus, Eqs. (1)-(4) form a closed problem, describing the system evolution of the generated supercritical nuclei of the new phase without including the recondensation process, characteristic of the concluding stage of the phase transition.

The system of equations (1)-(4) includes two size parameters: the material diffusion coefficient D and the nucleation frequency J, determining the characteristic scales of time and length:

$$t_0 = \left[\Delta\eta(0)^{-3}\rho^3 D^{-3} J_0^{-2}\right]^{1/5},$$
$$l_0 = \left[\Delta\eta(0)\rho^{-1} D J_0^{-1}\right]^{1/5}, \quad J_0 \equiv J\left[\Delta\eta(0)\right].$$

Using t_0 and ℓ_0, we define dimensionless variables and parameters as

$$s = r/l_0, \quad \tau = t/t_0, \quad F(\tau, s) = l_0^4 f(t, r),$$
$$q = \frac{4}{3}\pi\frac{\rho}{\Delta\eta(0)}, \quad c(\tau) = \frac{\Delta\eta(t)}{\Delta\eta(0)}.$$

In the dimensionless variables the system of equations (1)-(4) is

$$\frac{\partial F}{\partial\tau} + c(\tau)\frac{\partial}{\partial s}\left(\frac{F}{s}\right) = B_0 c(\tau)\frac{\partial^2 F}{\partial s^2}; \tag{5}$$

$$c(\tau)\left[\frac{F}{s} - B_0\frac{\partial F}{\partial s}\right]_{s=0} = \frac{J(c)}{J_0}; \tag{6}$$

$$F(0, s) = 0, \quad ds/d\tau = c(\tau)/s; \tag{7}$$

$$c(\tau) = 1 - q\int_0^\infty s^3 F(\tau, s)\,ds, \quad c(0) = 1. \tag{8}$$

Analogously [18] let us introduce new functions

$$u(\tau, s) = \frac{F(\tau, s)}{s}, \quad \Theta(\tau) = \int_0^\tau c(\tau)\,d\tau. \tag{9}$$

Using (9) in (5)-(7), the following boundary value problem is obtained for the function u

$$\frac{\partial u}{\partial\Theta} + \frac{1}{s}(1 - 2B_0)\frac{\partial u}{\partial s} = B_0\frac{\partial^2 u}{\partial s^2},$$

$$u(s, 0) = 0, \quad \left[u\left(\frac{1}{B_0} - 1\right) - s\frac{\partial u}{\partial s}\right]_{s=0} = \frac{J[c(\tau)]}{B_0 c(\tau) J_0},$$

which is conveniently solved by means of the Laplace transformation in the variable Θ. Denoting by the subscript p the Laplace transform of the corresponding quantities, we have the equation

$$\frac{d^2u_p}{ds^2}+\left(2-\frac{1}{B_0}\right)\frac{1}{s}\frac{du_p}{ds}-\frac{p}{B_0}u_p=0, \tag{10}$$

$$\left[\left(\frac{1}{B_0}-1\right)u_p-s\frac{du_p}{ds}\right]_{s=0}=\frac{1}{B_0J_0}\left[\frac{J(c)}{c(\tau)}\right]_p,$$

representing a Bessel equation [19], whose general solution is

$$u_p(s)=s^{\nu}\left[C_1I_{\nu}\left(s\sqrt{\frac{p}{B_0}}\right)+C_2K_{\nu}\left(s\sqrt{\frac{p}{B_0}}\right)\right],$$

where $I_{\nu}(x)$ and $K_{\nu}(x)$ are the Bessel function of an imaginary argument and the Macdonald function, and $\nu = (1/B_0 - 1)/2$.

Using the obvious condition of absence of a separate infinitely large radius, i.e., $u_p(\infty) = 0$, we obtain $C_1 = 0$, since the function $I_{\nu}(x)$ is increasing without bound. Determining the coefficient C_2 from the boundary condition (10), for the transform $u_p(s)$ we find the solution

$$u_p(s)=\frac{\left(s\sqrt{\frac{p}{B_0}}\right)^{\nu}K_{\nu}\left(s\sqrt{\frac{p}{B_0}}\right)}{2^{\nu}\Gamma(\nu+1)B_0J_0}\left[\frac{J(c)}{c(\tau)}\right]_p.$$

Performing the inverse transformation on the basis of [19]

$$L_{\Theta}^{-1}\left[\left(\frac{p}{\alpha}\right)^{\nu/2}K_{\nu}(2\sqrt{\alpha p})\right]=\frac{\exp(-\alpha/\Theta)}{2\Theta^{\nu+1}},$$

for the distribution function $F(\tau, s)$ we have the solution

$$F(\tau,s)=\frac{s^{2\nu+1}}{2^{2\nu+1}\Gamma(\nu+1)B_0^{\nu+1}}\int\limits_0^{\Theta(\tau)}\frac{J[c(\xi)]}{c(\xi)J_0}\exp\left\{-\frac{s^2}{4B_0[\Theta(\tau)-\xi]}\right\}\frac{d\xi}{[\Theta(\tau)-\xi]^{\nu+1}}. \tag{11a}$$

When $B_0 = 0$ the solution of Eq. (5) is easily obtained by means of the method of characteristics

$$F(\tau,s)=su_1\left[\Theta(\tau)-\frac{s^2}{2}\right]H\left[\Theta(\tau)-\frac{s^2}{2}\right], \tag{11b}$$

where $H(x)$ is the Heaviside function, and $u_1[\Theta(\tau)]$ satisfies condition (6)

$$u_1[\Theta(\tau)]=J[c(\tau)]/c(\tau)J_0. \tag{12}$$

To use these solutions it is necessary to know the functional dependence of the dimensionless supersaturation $c(\tau)$ on the function $\Theta(\tau)$, determined in (9). This dependence can be obtained by substituting $F(\tau, s)$ in the balance equation. Using then (11a) in (8), and integrating over the variable s, we have an integral equation describing the kinetics of supersaturation removal:

$$c[\Theta(\tau)]=1-Q_1(B_0)\int\limits_0^{\Theta(\tau)}[\Theta(\tau)-\xi]^{3/2}\frac{J[c(\xi)]}{c(\xi)J_0}d\xi,\quad Q_1(B_0)=8qB_0^{3/2}\frac{\Gamma(\nu+2{,}5)}{\Gamma(\nu+1)}. \tag{13a}$$

An equation similar in structure [13, 14] is also obtained for solving (11b), (12):

$$c[\Theta(\tau)]=1-Q_1(0)\int\limits_0^{\Theta(\tau)}[\Theta(\tau)-\xi]^{3/2}\frac{J[c(\xi)]}{c(\xi)J_0}d\xi,\quad Q_1(0)=2\sqrt{2}q\equiv Q. \tag{13b}$$

By the same method one can reach an equation describing the time dependence of the mean separation radius $\langle s(\tau)\rangle$:

$$\langle s(\tau)\rangle=\frac{Q_2(B_0)}{n(\tau)}\int\limits_0^{\Theta(\tau)}\sqrt{\Theta(\tau)-\xi}\,\frac{J[c(\xi)]}{c(\xi)J_0}d\xi, \tag{14}$$

$$Q_2(B_0)=\sqrt{2}B_0\frac{\Gamma(\nu+1{,}5)}{\Gamma(\nu+1)},\quad Q_2(0)=\sqrt{2}.$$

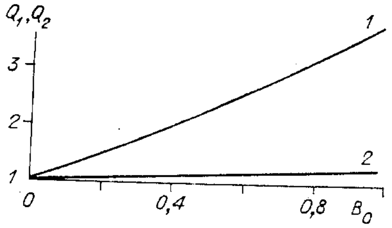

Fig. 1

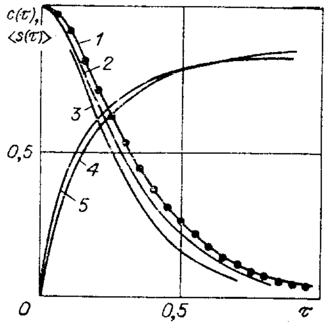

Fig. 2

Here

$$n(\tau) \equiv l_0^3 N(t) = \int_0^\infty F(\tau, s)\, ds = \int_0^{\Theta(\tau)} \{J[c(\xi)]/c(\xi) J_0\}\, d\xi$$

is the formation number of the new phase in a volume of size ℓ_0^3.

It follows from analyzing expressions (13) and (14) that the effect of fluctuations on the integral characteristics of the process is basically reduced to the appearance of the coefficients $Q_1(B_0)$ and $Q_2(B_0)$, whose dependences on B_0 are shown in Fig. 1. Since the quantity Q_1 (curve 1) is larger than $Q_1(0)$, the presence of fluctuations in the growth rate of identical size extractions leads to a substantially faster drop in supersaturation [see (13a) and (13b)]. The quite weak B_0-dependence of the coefficient Q_2 (curve 2) implies that the mean size of formation of the new phase is practically unchanged in the presence of weak fluctuations (i.e., when $B_0 < 1$). The following asymptotic result ($B_0 \ll 1$) is valid for low fluctuation intensities

$$Q_1 = Q\left(1 + \frac{9}{4} B_0\right), \quad Q_2 = \sqrt{2}\left(1 + \frac{1}{4} B_0\right).$$

Further analysis of the process requires solution of the supersaturation equation (13). Within the context of its nonlinear functional character, obtaining an exact solution is practically out of the question. However, the presence of the nucleation frequency J(c) in the integral of (13), sharply decreasing the supersaturation function, makes it possible to construct approximate time dependences of the supersaturation function. On this basis were solved problems of phase transition kinetics by the integral method [10-12] and by the Laplace method [8, 9], developed for the kinetic regime of separation growth. Due to features of the higher derivatives of the supersaturation with respect to time at the moment $\tau = 0$ for the investigated diffusion regime (3), the Laplace method is not applicable, since the following asymptotic dependences follow from (13) for short times

$$c(\xi) \approx 1, \quad J[c(\xi)] \approx J_0, \quad c[\Theta(\tau)] = 1 - \frac{2}{5} Q_1(B_0)\, \Theta(\tau)^{5/2}. \tag{15}$$

At the same time the behavior of the higher derivatives $c^{(n)}(\tau)$ at the point $\tau = 0$ is determined by the nonanalytic dependence

$$c(\tau) = 1 - (2/5) Q_1(B_0)\, \tau^{5/2},$$

following from (15).

The construction of an approximate (and quite accurate) solution for problem (1)-(4) is nevertheless possible, and is considered below on the example of Frenkel'-Zel'dovich nucleation kinetics [20], for which [9, 13, 20]

$$\frac{J[c(\tau)]}{c(\tau) J_0} = \exp[P g(\tau)], \quad g(\tau) = 1 - c(\tau)^{-2} \leqslant 0.$$

The parameter P appearing here is the dimensionless activation energy of the generation process of a critical nucleus, referring to the square of the initial supersaturation [9, 13, 20]. In real situations this quantity is quite large (P ~ 5-100). The function $g(\tau)$ decreases from its maximum value $g(0) = 0$ to $-\infty$ when $\tau \to \infty$. Therefore, $\exp[Pg(\tau)]$ is a rapidly vanishing function. This implies that the basic contribution to the integral in (13) is provided by a close vicinity of $\xi = 0$. Expanding in a Maclaurin series in the variable ξ the slowly varying integrand function $[\Theta(\tau) - \xi]^{3/2}$, the following dependence is obtained

$$c[\Theta(\tau)] = 1 - Q_1\Theta(\tau)^{3/2}\int\limits_0^{\Theta(\tau)} \exp[Pg(\xi)]\,d\xi + \frac{3}{2}Q_1\Theta(\tau)^{1/2}\int\limits_0^{\Theta(\tau)} \xi\exp[Pg(\xi)]\,d\xi + \ldots \tag{16}$$

Assuming that the corresponding integrals in (16) converge quite quickly, we let the upper integration limit $\Theta(\tau)$ tend to infinity, and use for $c(\xi)$ the short-time asymptote (15). As a result, the following approximate dependence is valid for quite long times following the beginning of the process

$$c[\Theta(\tau)] = 1 - \varepsilon_1\Theta(\tau)^{3/2} + \varepsilon_2\Theta(\tau)^{1/2} + \ldots, \qquad \varepsilon_1 = Q_1\int\limits_0^{\infty}\exp[Pg(\xi)]\,d\xi, \quad \varepsilon_2 = \frac{3}{2}Q_1\int\limits_0^{\infty}\xi\exp[Pg(\xi)]\,d\xi. \tag{17}$$

The coefficients ε_i can be calculated numerically or approximately by the substitution (15):

$$\exp[Pg(\xi)] = \exp\{P[1 - c(\xi)^{-2}]\} = \exp\left\{P\left[1 - \left(1 - \frac{2}{5}Q_1\xi^{5/2}\right)^{-2}\right]\right\} \approx \exp\left(-\frac{4}{5}PQ_1\xi^{5/2}\right). \tag{18}$$

Then

$$\varepsilon_1 = Q_1\frac{\Gamma(1{,}4)}{(PQ_1)^{2/5}}\left(\frac{5}{4}\right)^{2/5} = 0{,}9701\left(\frac{Q_1^3}{P^2}\right)^{1/5}, \qquad \varepsilon_2 = \frac{3}{2}Q_1\frac{\Gamma(1{,}8)}{(PQ_1)^{4/5}}\left(\frac{5}{4}\right)^{4/5} = 0{,}83506\left(\frac{Q_1}{P^4}\right)^{1/5}. \tag{19}$$

On the basis of Eqs. (9) and (17) one obtains for the function $\Theta(\tau)$ a differential equation, whose solution with the obvious condition $\Theta(0)=0$ is

$$\frac{d\Theta}{d\tau} = 1 - \varepsilon_1\Theta^{3/2} + \varepsilon_2\Theta^{1/2}, \quad \tau = \int\limits_0^{\Theta(\tau)}\frac{d\Theta}{1 - \varepsilon_1\Theta^{3/2} + \varepsilon_2\Theta^{1/2}}. \tag{20}$$

From (18) we can obtain a lower bound for which (17)-(20) holds:

$$\Theta(\tau) \geqslant \left(\frac{4}{5}PQ_1\right)^{-2/5} \ll 1.$$

It is necessary to note that continuation of the series (17) leads to the appearance of terms with negative powers $\Theta^{-n/2}$ $(n = 1, 3, \ldots)$, diverging when $\tau \to 0$. In this case, however, the transition conditions from (16) to (17) are violated, and it cannot be assumed that the coefficients ε_i are independent of τ. Inclusion of the latter provides a correct, but somewhat unwieldy mathematical problem. To sum up, expressions (17)-(20) determine the time dependence of the dimensionless supersaturation in the form of an implicit function. The comparison shown in Fig. 2 with the numerical solution (points, $B_0 = 0$) of Eq. (13) shows that the approximate solution (curve 1, $B_0 = 0$) is quite accurate. The deviation from the numerically calculated $c(\tau)$ value does not exceed 3% in the whole time interval, while the accuracy is enhanced with increasing parameter P. The supersaturation drops more quickly (curves 2, 3 for $B_0 = 0.1$ and 0.3) with increasing fluctuation intensity (i.e., increasing B_0).

One must also note a certain universality in the dependence $c[\Theta(\tau)]$ when in (17) one replaces $\Theta(\tau)$ by the function $Q_1^{2/5}\Theta(\tau)$.

A similar approximate estimate can also be selected for the mean separation radius of the new phase

$$\langle s(\tau)\rangle = Q_2\Theta(\tau)^{1/2} - \frac{0{,}26243\,Q_2}{(PQ_1)^{2/5}}\Theta(\tau)^{-1/2}.$$

The characteristic dependences $\langle s(\tau)\rangle$ are shown in Fig. 2, where curves 4, 5 correspond to $B_0 = 0$ and 0.3. Since the mean radius characterizes the drop rate of supersaturation, at the initial portion of the curve the presence of fluctuations leads to somewhat larger values of the mean radius of separation. On a finite portion the dependence of $\langle s(\tau)\rangle$ on B_0 provides an opposite effect, in agreement with the behavior of the curves $c(\tau)$ for different B_0.

The temporal flow evolution of the radial distribution function (11a) is shown in Fig. 3 ($B_0 = 0.1$, curves 1-4 correspond to increasing time τ). It is seen that the distribution is Gaussian, as is the case for the kinetic regime [5, 7], with dispersion

$$\langle D\rangle = \left[\frac{2(B_0+1) - Q_2^2}{n(\tau)}\right]\left[\Theta(\tau) - \frac{0{,}52486}{(PQ_1)^{2/5}}\right] + \Theta(\tau)^{-1}\frac{Q_2^2}{n(\tau)}\frac{0{,}04427}{(PQ_1)^{4/5}} + \ldots,$$

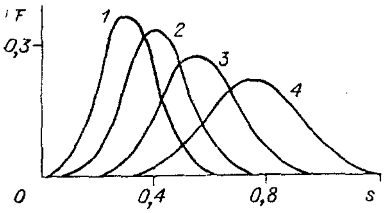

Fig. 3

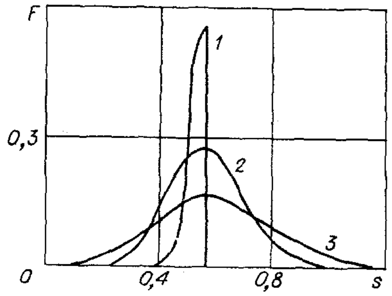

Fig. 4

$$B_0 \ll 1,\quad \langle D\rangle = \frac{B_0}{n(\tau)}\left[\Theta(\tau) - \frac{0{,}52486}{(PQ)^{2/5}}\right] + \Theta(\tau)^{-1}\frac{0{,}08854}{n(\tau)\,(PQ)^{4/5}}(1-1{,}3B_0).$$

The effect of the diffusion growth regime (3) consists of a drift in the distribution curve toward larger radii which is nonuniform with the flow of time, as satisfied for the kinetic regime. With increasing fluctuation intensity of the growth rate (i.e., increasing B_0) the distribution curve is more spread out (Fig. 4) for a practically nonvarying mean radius (curves 1-3 correspond to B_0 = 0, 0.1, 0.3). Generally speaking, the results on the evolution of the distribution function are the expected ones. This follows from the properties of the evolutionary Fokker–Planck equation (1) utilized, recalling (for B_0 independent of r) the equation of convective diffusion in the space of separation radii.

Note that it follows from the analysis of the problem that the separation kinetics of the new phase is determined by the initial time portion, i.e., by the nucleus formation process. It is precisely on this basis that one uses the method of approximate solution of the supersaturation equation (13). In the given temporal region, however, the characteristic formation radius of the new phase is comparable in magnitude with the critical nucleus radius. Generally speaking, therefore, the commonly used assumption $r_* = 0$ is not always justified, since it corresponds to a time interval for which the effect of the boundary point $r = r_*$ is completely missing. The nature of the dependence $c(\tau)$ or $c[\Theta(\tau)]$ is obviously unchanged for finite small r_* values, but the coefficients ε_i are different.

This situation requires further studies, so that at long times and following the start of the phase transition, when supersaturation becomes small, the recondensation process starts exerting a substantial effect. The theory of system evolution of this stage, developed by I. M. Lifshitz and V. V. Slezov [20], describes the asymptotic behavior of infinite long times ($\tau \to \infty$). So far, however, the following problem remains unanswered: for what supersaturation values is it necessary to take into account recondensation? Since the recondensation effect is related to the effect of the boundary point $r = r_*(t)$, shifting with the flow of time to the region of large radii, the initial and concluding stages of the phase transition are effectively related between them, despite the difference in the physical processes determining the system behavior at each stage. In this connection it is, obviously, possible to relate with each other the stages of nucleus formation, the separation stage of the fundamental mass of the new phase and the recondensation phase, during subsequent account of the finiteness of the initial value of the critical nucleus radius.

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THERMODYNAMIC PROPERTIES AND THERMAL EQUATIONS OF THE STATE OF HIGH-PRESSURE ICE PHASES

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UDC 536.424

Water is characterized by a surprising number of phases compared to other materials [1, 2]. Of the solid phases (ices), the hexagonal ice I is thermodynamically stable under natural conditions on earth, while the others are high-pressure phases. Thermodynamic conditions for the existence of the high-pressure ices occur on several planets of the solar system and their satellites [3, 4]. The formation of various ice modifications has been observed in studying explosive impact loading of ice I. In this case a very complex wave picture is observed, which is related to phase transitions between the various ice modifications, and also to melting behind the compression wave front at relatively low pressure (on the order of 10^2-10^3 MPa) [5, 6].

Within the frame work of the mechanics of continuous media, a theoretical description of the processes of quasi-static and dynamic deformation of ice is based on studying the thermodynamic properties of various ice modifications, water, and their mixtures [7-9]. Here we continue the investigation, started in [10] on ice I to pressures of 210 MPa. Based on a critical analysis of experimental data [2, 11-19], a corresponding theoretical study was made of the thermodynamic properties of ices I, III, V, and VI; thermal equations of state were constructed, which are applicable for temperatures of 233-293 K and pressures of 0-10^3 MPa.

1. H_2O Phase Diagram. In studying the thermodynamic properties of ices, we choose as independent variables the temperature T and the pressure p and the limits of their variation: $233 \leqslant T \leqslant 293$ K and $0 \leqslant p \leqslant 10^3$ MPa. The corresponding set of points on the p–T phase diagram we denote by Ω. The set Ω includes 1) the thermodynamically stable states of ices I,

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