INTERPOLATIONAL EQUATION OF STATE OF NaCl, TAKING ACCOUNT OF PROCESSES OF MELTING, VAPORIZATION, DISSOCIATION, AND IONIZATION

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INTRODUCTION

With the investigation of many problems in the mechanics of continuous media, geophysics, etc., for the mathematical closure of the problems under consideration there are needed equations of state of the continuous media, describing their thermodynamic properties in a wide region of states, including the crystalline, molten, vaporized, dissociated, and ionized states. In [1-3], methods are developed for the construction of interpolational equations of state, taking in the above regions, with the exception of the region of melting. For a number of substances, the melting process has a considerable energy consumption and cannot be neglected in applied calculations. The present article, using the example of NaCl, develops the basic concepts of [1, 2] and constructs an equation of state which takes account of all the abovementioned processes, including melting.

The principal difficulty in the way of constructing interpolational equations of state of this type is an adequate determination of the characteristic parameters in the supporting models of the medium [1-3] and in the interpolational functions. These difficulties are aggravated by the insignificant volume of experimental data on the thermodynamic properties of solid media. In the present article methods are developed for determining these parameters from the existing experimental data.

The description of melting processes requires the equations of state of the crystalline phase and the melt.

1. Equation of State of the Crystalline Phase of NaCl

For description of the crystalline state we use a known model of an ionic crystal [4], assuming that all the atoms vibrate with an identical frequency characterized by the Debye temperature Θ_D. Then, on the basis of the Debye model [4], we obtain

$$p = p_C(v) + \frac{6R}{M}\frac{\gamma\rho\Theta_D}{e^{\Theta_D/T}-1}; \tag{1.1}$$

$$E = E_C(v) + \frac{6R}{M}\frac{\Theta_D}{e^{\Theta_D/T}-1}; \tag{1.2}$$

$$E_C = -\int\limits_{v_k}^{v} p_C(v)\,dv, \tag{1.3}$$

where p_C and E_C are the pressure and the energy of the cold state; M is the molecular weight; R is the gas constant; T is the temperature; v is the specific volume; v_k is the specific volume at T = 0; and γ is the Grüneisen coefficient. Under these circumstances, the following well-known relationship holds:

$$\Theta_D = \Theta_0 \exp\left(\int\limits_{\rho_0}^{\rho} \frac{\gamma}{\rho}\,d\rho\right), \tag{1.4}$$

where Θ_0 is the Debye temperature at normal density ρ_0. From (1.1)-(1.4) it follows that for a description of the state of the crystalline phase, we must determine $\gamma(\rho)$, Θ_0, and $p_C(\rho)$.

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It is known in [5] that the known schemes for a theoretical determination of the Grüneisen coefficient (the Landau–Slater, Dugdale–McDonald, and "free volume" approximations) lead to considerable errors. Therefore, in the present work the dependence $\gamma(\rho)$ was constructed on the basis of known thermodynamic identities [6] connecting the Grüneisen coefficient with the isobaric heat capacity, the modulus of volumetric compression, and the coefficient of thermal expansion. The data on these parameters were taken from [7, 8]. They took in a range of change in the density (1.9-2.2). It is well known [9] that the following relationship holds in the vicinity of ρ_0:

$$\gamma = \gamma(\rho_0)\rho_0/\rho,$$

In limiting cases

$$\lim_{\rho\to\left\{\begin{smallmatrix}\infty\\0\end{smallmatrix}\right.} \gamma = \frac{2}{3}.$$

On the basis of these data, the interpolational dependence was constructed:

$$\gamma = \frac{2}{3} + \frac{4.12\rho^2}{\rho^4 + 1.16}, \tag{1.5}$$

where ρ is in g/cm^3.

From (1.4) and (1.5) we obtain

$$\Theta_D = \Theta_0 (\rho/\rho_0)^{2/3} \exp\left[1.92 \operatorname{arctg} \frac{1.08\,(\rho^2 - \rho_0^2)}{1.16 + \rho_0^2\rho^2}\right], \tag{1.6}$$

where it is assumed that $\Theta_0 = 300$°K (see, for example, [5, 6]).

The pressure of cold compression was determined in two steps. In the region of elongations it was represented analogously [1, 2] in the form

$$p_C = A(\delta^m - \delta^n) \text{ for } \delta = \rho/\rho_k < 1. \tag{1.7}$$

The parameters A, m, and ρ_k were calculated on the basis of the known volumetric velocity of sound $c_0(p_0, T_0) = 3.33$ km/sec, energy of sublimation $Q_S = 3.94 \cdot 10^{10}$ ergs/g [7], and the equality (1.1) for $p = p_0$, $T = T_0$, and $\rho = \rho_0$. The value of n was selected on the basis of the best agreement between the experimental data of [8] on $\rho(T)$ for $p = p_0$ and calculated data, computed from (1.1) and (1.7). As a result we obtain $A = 13.1 \cdot 10^{10}$ dyn/cm^2, $\rho_k = 2.206$ g/cm^3, $m = 4$, and $n = 2$.

In the region of compression, p_C was determined using experimental data on the dynamic compressibility [10-13] and the Thomas–Fermi cold model of an atom for large degrees of compression. The results of the calculations are given in Table 1.

Thus, the relationships (1.1)-(1.3), (1.5)-(1.7), and Table 1 completely determine the state of the crystalline phase. A comparison of the isobaric heat capacities, calculated on the basis of this equation of state and the data of [7], shows their good agreement.

2. Equation of State of the Melt

The equation of state of the melt must assure the subsequent transition of the substance into the vaporized, dissociated, and ionized states. Therefore, to construct it we use the approach of [1-3]. In terms of the free energies, we represent the interpolational equation of state of the melt in the form

$$F = F_C + \frac{RT}{M}\ln(1 + z_1^{n_1})^{1/n_1} - \frac{RT}{M}\ln(1 + z_2^{n_2})^{1/n_2}, \tag{2.1}$$

where

$$F_C = E_C + Q_0 + \frac{6RT}{M}\ln(1 - e^{-\Theta_D/T}) + F_e \tag{2.2}$$

for the condensed phase.

TABLE 1

ρ, g/cm³	2,27	2,38	2,60	3,03	3,46	3,89	4,33	4,56	5,19	5,62
p_C, mbar	0,0079	0,023	0,060	0,17	0,33	0,54	0,79	1,20	1,82	2,09

In (2.2), along with the cold and hot components of the state, there are included the component of the thermal excitation of the electrons F_e and the energy Q_0, equal to the difference in the sublimation energies of the crystalline and liquid phases, which has the nominal meaning of the melting energy at T = 0 [2]. In (2.1), z_1 and z_2 for the free energy of the condensed state go over consecutively into the free energies of the vaporized (F_g) and dissociated (F_d) states [4, 6]:

$$\begin{aligned} F_g &= E_C + Q_0 + \frac{RT}{M}\ln\left[\left(\frac{h^2}{2\pi m_1 kT}\right)^{3/2}\frac{N}{ev}\frac{\Theta_r\Theta_1}{T^2}\right] - \frac{RT}{M}\ln z_{e_1} + F_e, \\ F_d &= E_C + Q_0 + \frac{RT}{M}\ln\left(\frac{h^2N^{2/3}}{2\pi m_2^{1/2}m_3^{1/2}e^{3/2}v^{2/3}kT}\right)^3 - \frac{RT}{M}\ln(z_{e_2}z_{e_3}) + F_e, \end{aligned} \tag{2.3}$$

where h and k are the Planck and Boltzmann constants; m_i and z_{e_i} (i = 1, 2, 3) are the masses of the particles and the electronic statistical sums, respectively, for NaCl, Na, and Cl; Θ_r = 0.314°K and Θ_1 = 525°K are the temperatures characterizing the rotation of the molecule and the vibrations of the atoms in the molecule; and N is the number of particles in the volume v.

Examining consecutively the asymptotic in (2.1) for $z_1 \gg 1$ and $z_2 \gg 1$, we obtain

$$z_1 = a_1 v^{6\gamma-1}T^{5/2}; \tag{2.4}$$

$$z_2 = \begin{cases} a_2 v T^{-0.5}\exp\left(-\dfrac{Q_d M}{RT}\right) & \text{for} \quad T \leqslant \dfrac{2Q_d M}{R} = 10^5\,°\text{K}, \\ a_2 v \cdot 10^{-2,5}\exp(-0.5) & \text{for} \quad T > 10^5\,°\text{K}; \end{cases} \tag{2.5}$$

$$a_1 = \left(\frac{h^2}{2\pi k}\right)^{3/2}\left(\frac{N_A}{M_1}\right)^{5/2}\frac{\Theta_r\Theta_1}{e\Theta_0^6}\rho_0^{6\gamma} \approx 0.95\cdot 10^{-11}; \tag{2.6}$$

$$a_2 = \left(\frac{2\pi k}{h^2}\right)^{3/2}\left(\frac{M_2^3M_3^3}{M_1}\right)^{1/2}\frac{e\Theta_r\Theta_1}{N_A^{5/2}}\frac{g_2g_3}{g_1} \approx 3{,}42\cdot 10^3. \tag{2.7}$$

In obtaining (2.4)-(2.7), the following relationships were used [6]:

$$\frac{z_{e_2}z_{e_3}}{z_{e_1}} = \frac{g_2g_3}{g_1}e^{-Q_d/RT}, \quad m_i = \frac{M_i}{N_A},$$

where M_i is the molecular (atomic) weight of the i-th particle; g_i is the statistical weight of the ground state of the i-th particle (g_1 = 1, g_2 = 2, and g_3 = 4 [7]); N_A is Avogadro's number; and $Q_d = 7\cdot 10^{10}$ ergs/g is the dissociation energy. In view of the lack of experimental data, in (2.4) the Grüneisen coefficient was assumed constant. In this case the Debye temperature is expressed in terms of the density in the form

$$\Theta_D = \Theta_0(\rho/\rho_0)^\gamma, \tag{2.8}$$

where ρ_0 = 1.549 is the density of the melt at normal pressure [8]; Θ_0 = 132°K (a method for calculating this value is given below).

Thus, on the basis of the interpolation carried out, from (2.1)-(2.4), we obtain the following expressions for the pressure and the internal energy of the melt:

$$p = p_C + \frac{6R}{M}\frac{\gamma\rho\Theta_D}{e^{\Theta_D/T}-1} - \frac{RT}{Mv}\left[\frac{(6\gamma-1)z_1^{n_1}}{1+z_1^{n_1}} - \frac{z_2^{n_2}}{1+z_2^{n_2}}\right] + p_e; \tag{2.9}$$

$$E = E_{\mathrm{C}} + \frac{6R}{M}\frac{\Theta_D}{e^{\Theta_D/T}-1} - \frac{5}{2}\frac{RT}{M}\frac{z_1^{n_1}}{1+z_1^{n_1}} + \left(Q_{\mathrm{d}} - \frac{RT}{2M}\right)\frac{z_2^{n_2}}{1+z_2^{n_2}} + Q_0 + E_e. \tag{2.10}$$

For complete closing of the thermodynamic description in (2.8)-(2.10), it is necessary to determine Θ_0, γ, n_1, n_2, and the functions p_{C}, E_{C} and p_e, E_e. We turn to an examination of this question.

We shall describe the electronic components of state using the dependences [1]

$$\begin{gathered}
p_e = \frac{452z^{1/3}T^2(vM)^{-1/3}}{1+5.45\cdot 10^{-6}z^{-2/3}(vM)^{2/3}T}\left[1+\frac{7.35\cdot 10^{-2}(zMv)^{1/2}}{1+4.2\cdot 10^{-10}vMT^{3/2}}\right]^{-1}\Phi\ \mathrm{dyn/cm^2},\\
E_e = p_e v\left[\frac{3}{2}+\frac{3.3\cdot 10^{-5}(zMv)^{1/3}(T^{8/9}z^{-32/27}+3.34\cdot 10^3)}{1+3.43\cdot 10^{-7}z^{-2}T^{3/2}+1.02\cdot 10^{-8}z^{-1/3}MvT}\right]f\ \mathrm{ergs/g},\\
\Phi = \frac{vT^3}{vT^3+10^{12}},\quad f = 1+\frac{3.78\cdot 10^5(zMv)^{-0.261}z^{4/3}T^2}{[T+2.46\cdot 10^5 z^{4/3}(zMv)^{-0.223}]^3},
\end{gathered} \tag{2.11}$$

where $z = 14$ and $M = 29.2$ are the mean charge number and the molecular weight of NaCl. In distinction from [1], the factor Φ is introduced into (2.11), assuring the damping of the electronic components with a lowering of the temperature to levels at which the thermal excitation of the electrons in real media becomes negligibly small.

At the present time there are no data on the Debye temperature Θ_0 for a melt. To evaluate this quantity we use an indirect method. Let us consider the state of a melt at p_0 = 1 bar and $T = T_{\mathrm{mt}}$ = 1073°K.

It is obvious that under these conditions in the equation of state we can neglect terms connected with vaporization, dissociation, and electronic excitation. Taking account of what has been said, the internal energy of the melt can be represented directly in terms of the energy of the crystalline phase in the form

$$E_{\mathrm{C}} = \overset{\mathrm{m}}{E_{\mathrm{C}}} + \overset{\mathrm{m}}{E_T} + Q_0 = \overset{\mathrm{c.p}}{E_{\mathrm{C}}} + \overset{\mathrm{c.p}}{E_{\mathrm{T}}} + L_0 - p_0(\overset{\mathrm{m}}{v_0} - \overset{\mathrm{c.p}}{v_0}), \tag{2.12}$$

where the superscripts m and c.p relate, respectively, to the melt and the crystalline phase; and $L_0 = 4.89\cdot 10^9$ ergs/g is the latent energy of melting. Using the equalities of the Gibbs energies at the curve of the melting,

$$F^{\mathrm{c.p}} + p_0 v_0^{\mathrm{c.p}} = F^{\mathrm{m}} + p_0 v_0^{\mathrm{m}}$$

and expressions for the free energies of the type of (2.2), from (2.12) we obtain an equation in the form

$$\begin{gathered}
L_0 = \frac{6RT}{M}\left\{\ln\frac{1-\exp(-\Theta_D^{\mathrm{c.p}}/T_{\mathrm{mt}})}{1-\exp(-\Theta_D^{\mathrm{m}}/T_{\mathrm{mt}})} - \frac{\Theta_D^{\mathrm{m}}/T_{\mathrm{mt}}}{1-\exp(\Theta_D^{\mathrm{m}}/T_{\mathrm{mt}})} + \right.\\
\left. + \frac{\Theta_D^{\mathrm{c.p}}/T_{\mathrm{mt}}}{1-\exp(\Theta_D^{\mathrm{c.p}}/T_{\mathrm{mt}})}\right\} \approx \frac{6RT}{M}\ln\frac{1-\exp(-\Theta_D^{\mathrm{c.p}}/T_{\mathrm{mt}})}{1-\exp(-\Theta_D^{\mathrm{m}}/T_{\mathrm{mt}})}.
\end{gathered} \tag{2.13}$$

From (1.1) for p_0 = 1 bar and $T = T_{\mathrm{mt}}$ we obtain $\rho_0^{\mathrm{c.p}} = 1.87$ g/cm³, and from (1.6) we determine $\Theta_D^{\mathrm{c.p}}(\rho_0^{\mathrm{c.p}})$ = 237°K. On the basis of these data, from (2.13) we obtain $\Theta_D^{\mathrm{m}} = \Theta_0$ = 132°K.

In view of the lack of the required experimental data, for determining the Grüneisen coefficient we use the following approach. At $T = T_{\mathrm{mt}}$ and $p = p_0$, the coefficient of thermal expansion $\alpha = 3.67\cdot 10^{-4}$ 1/deg [8] and the heat capacity $C_p = 1.148\cdot 10^7$ ergs/(g·deg) [7] of the melt are known.

Neglecting in (2.10) terms characterizing vaporization, dissociation, and ionization, on the basis of the relationship

$$C_p = \partial E/\partial T|_p$$

we have the expression

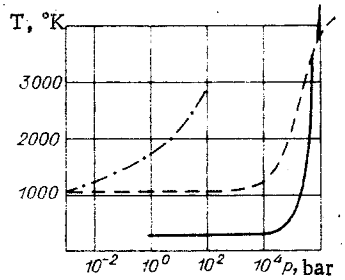

Fig. 1

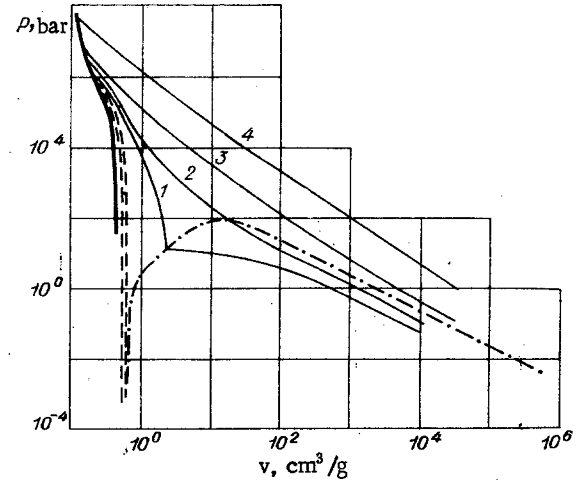

Fig. 2

TABLE 2.

ρ, g/cm³	2,04	2,25	2,60	3,01	3,66	4,45	5,41	6,58	8,00	9,25	10,7	12,4
p_C, mbar	0,031	0,064	0,12	0,23	0,47	0,93	1,78	3,60	7,10	11,7	18,2	27,4

TABLE 3

p, bar	10^{-3}	10^{-2}	10^{-1}	1	2	4	10	20	50	84,7
T, °K	1075	1263	1465	1725	1825	1947	2153	2347	2667	2890
v^m, cm³/g	0,622	0,650	0,694	0,819	0,971	1,47	2,23	2,96	4,83	11,5
v^g, cm³/g	$2{,}95\cdot10^{6}$	$2{,}32\cdot10^{5}$	$2{,}23\cdot10^{4}$	2457	1275	658	268	130	42,3	11,5

$$\gamma = \frac{1}{\alpha\varphi^2 \exp(\Theta_D/T)}\left\{\frac{C_p MT}{6R} - \frac{\varphi^2 \exp(\Theta_D/T)}{T}\right\}, \tag{2.14}$$

$$\text{where } \varphi = \Theta_D\,[\exp(\Theta_D/T) - 1]^{-1}.$$

From (2.14) for $T = T_{mt}$ and $p = p_0$, $\gamma = 0.865$.

Let us consider the question of the determination of p_C. In the region of elongations, we shall represent it in the form (1.7). By analogy with [5], we take $n = 4/3$. As has been shown by *a posteriori* evaluations, this value gives calculated regults corresponding satisfactorily to the experimental data on melting and vaporization. Variations of the value of n worsen this agreement. In distinction from the crystalline phase, in the present case c_0 and Q_S are unknown. Therefore, for determination of the parameters A, m, and ρ_k in (1.7) for the melt we use other conditions: the coefficient of thermal expansion $\alpha(p_0, T_{mt})$, the energy equality (2.12), and the equality (2.9) for $T = T_{mt}$, $p = p_0$, and $\rho = 1.549$ g/cm³, setting $z_1 = z_2 = p_e \equiv 0$. On the basis of these conditions, the following values of the parameters are obtained:

$$A = 2{,}2\cdot10^{10}\ \text{dyn/cm}^2;\ m = 7{,}42;\ \rho_k = 1{,}85\ \text{g/cm}^3. \tag{2.15}$$

In the region of compressions, p_C for the melt was constructed analogously to p_C for the crystalline phase. Here use was made of the experimental data of [10, 13] and of the Thomas–Fermi model of the atom, which is the same for the crystals and the melt. The results are given in Table 2.

Let us dwell on the selection of the values of the parameters n_1 and n_2 in (2.1). The set (a_1; n_1) controls the curve of the vaporization. Detailed calculations of this curve have shown that the best agreement of the calculated results with the existing experimental data on the boiling point [7, 14, 15] as well as with evaluations of the parameters at the critical point [7] is obtained for

$$a_1 = 1\cdot10^{-9},\ n_1 = 1/3. \tag{2.16}$$

A comparison of the results of calculations of the degree of dissociation in an ideal-gas state using the methods of chemical thermodynamics [7] with (2.1), (2.9), and (2.10) showed that they are in the best agreement with

$$a_2 = 3.4\cdot10^3,\ n_2 = 2/3. \tag{2.17}$$

Thus, relationships (2.1)-(2.5), (2.9)-(2.11), and (2.15)-(2.17), together with Table 2, completely determine the state of the melt.

3. Boundaries of Region of Vaporization

In view of the lack of expressions for the free energies of the electronic components of state, the curve of the boundary of the region of vaporization was plotted by analogy with [1, 2]. The results of the calculations are given in Table 3. The vaporization curve is shown in Figs. 1 and 2 (the dashed-dot lines are the vaporization curves, the dashed lines are the melting curves, and the solid line is the shock adiabat; lines 1-4 are isentropes).

4. Boundary of Melting Region

The boundary of the melting region is constructed using the conditions of the equality of the Gibbs energies, the pressures, and the temperatures of the crystalline phase and the melt. Neglecting the electronic component of state, within the framework of the adopted model of NaCl we represent these conditions in the form

$$E_C^{m} - E_C^{c.p} + Q_0 + p\left(v^{m} - v^{c.p}\right) - \frac{6RT}{M}\ln\frac{1-\exp\left(-\Theta_D^{c.p}/T\right)}{1-\exp\left(-\Theta_D^{m}/T\right)} + \frac{RT}{M}\ln\frac{\left(1+z_1^{n_1}\right)^{1/n_1}}{\left(1+z_2^{n_2}\right)^{1/n_2}} = 0.$$

It must be noted that the value $Q_0 = 0.54\cdot10^{10}$ ergs/g, obtained on the basis of (1.7) and (2.15), gives $T_{mt} = 1200$°K, which differs from the experimental value $T_{mt} = 1073$°K. With a rise in the pressure and the temperature the role of this correction decreases rapidly. The results of calculations of the melting curve are given in Table 4 and in Figs. 1-3 (dashed lines).

From Figs. 1 and 2 it can be seen that the calculations in the region of low pressures are carried up to the intersection of the melting curve with the vaporization curve. In the region of lower pressures the model constructed is not acceptable, since the equations of state (1.1) and (1.2) do not describe a direct transition from the crystalline to the sublimed state.

An analysis of Figs. 1 and 3 and Table 4 shows that with a rise in the pressure up to values of ~1 kbar, the melting point does not vary by more than 3%; it increases sharply (by almost two times) in the region of pressures 10^4-10^6 bar and then approaches some asymptote $T_{mt} \approx 4100$°K. The jump in the specific volume decreases with a rise in the pressure, tending to zero. This latter circumstance is explained by the existence of an asymptote for the temperature, using the Clausius–Clapeyron equation:

$$dT_{mt}/dp = (v^{m} - v^{c.p})/(s^{m} - s^{c.p}).$$

Since the jump in the entropy always differs from zero, we have the asymptotic independence of the melting point from the pressure.

Thus, the interpolational model constructed makes it possible to obtain a rather complete representation of the character of the phase transitions in a wide range of states. To illustrate its reliability let us make some comparisons with known data on melting and shock compressibility.

Figure 3 gives a comparison between the melting curve and data calculated using the Simon formula (dashed–dot line)

$$p = A\left[(T/T_0)^c - 1\right]$$

TABLE 4

p, bar	10^{-3}	1	128	$1{,}02\times 10^3$	$8{,}2\cdot 10^3$	$3{,}4\cdot 10^4$	$1{,}1\cdot 10^5$	$3{,}1\cdot 10^5$	$5{,}5\cdot 10^5$	$1{,}1\cdot 10^6$	$1{,}9\cdot 10^6$
T, °K	1075	1075	1079	1100	1231	1560	2377	3160	3500	3851	4058
$v^{c.p}$, cm^3/g	0,536	0,536	0,536	0,534	0,514	0,464	0,392	0,314	0,267	0,222	0,186
v^m, cm^3/g	0,622	0,622	0,620	0,612	0,566	0,514	0,420	0,324	0,273	0,223	0,186

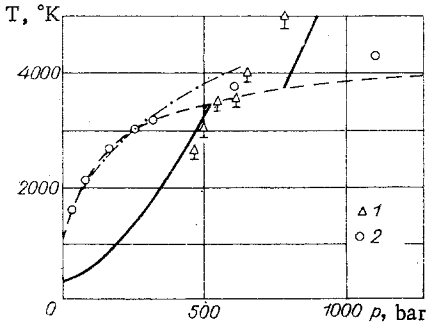

Fig. 3

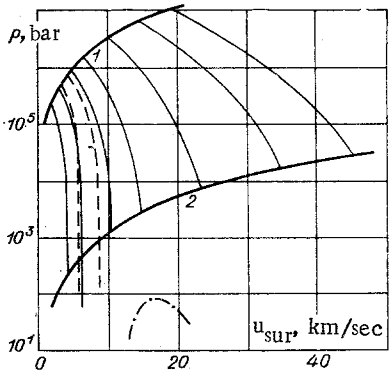

Fig. 4

with the Clark parameters [14]: A = 1.67 kbar, T_0 = 1073°K, C = 2.7, and p ≤ 20 kbar. The same figure gives calculated data [10] on the melting curve (1 represents calculated points). In addition, Fig. 3 gives a calculated shock adiabat (solidline) and analytical data on it from [10] (2 represents experiment). We note that the selection of the characteristic constants of the equations of state in the present work and in [10] rested on exactly the same experimental data on the melting curve and the dynamic compressibility. The difference is that in [10] an equation of state of the Mie—Grüneisen type was used, which does not take account of vaporization or of other processes taking place with high states, while the cold parts of the state were assumed to be identical for the melt and the crystalline phase. The regions of elongations and high degrees of compression were excluded from the discussion.

5. General Analysis of Results

Let us examine the behavior of the shock adiabat (the heavy line in Figs. 1-3) and the isentropes in the region of homogeneous and two-phase states.

The shock adiabat intersects the boundary between the two-phase crystal—melt states (see Fig. 3) at the points (530 kbar; 3480°K) and (780 kbar; 3700°K).

The results of calculations showed that along the left-hand boundary of the melting, the entropy increases monotonically with a rise in the pressure. This means that, with unloading, the isentropes go out from the region of the crystalline state into the region of a partial melt; i.e., there is partial melting.

At the right-hand boundary, with a rise in the pressure approximately up to 1 kbar the entropy remains practically constant, i.e., this segment of the boundary of the two-phase region is close to the isentrope. With a further increase in the pressure, the entropy rises, i.e., with unloading there is the possibility of the complete melting of a particle.

Qualitatively, there is a different picture at the boundary of the vaporization (see Fig. 2). In this case, with a rise of the pressure at the right- and left-hand branches of the boundary, there is a rise in the entropy. This is evidence that, with unloading, along the isentropes lying to the left of the "critical isentrope," particles go over from the condensed state into the two-phase state and, with unloading, to the right of the critical isentrope the particles go over from the gaseous state to the two-phase state. Another characteristic is the presence of a sharp point of inflection on the isentropes when they go from the region of the condensate into the region of the two-phase state, which is evidence of a large discontinuity in the velocity of sound. Evaluations show that the left-hand limit of

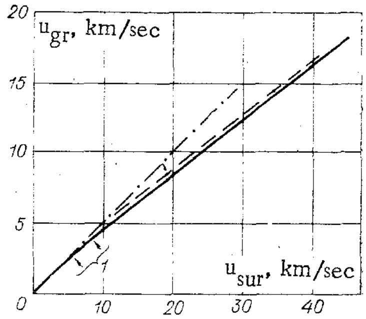

Fig. 5

the velocity of sound is on the order of 10^3 m/sec, while the limit on the right is (10^2-10^1) m/sec. This argues that the regions of the start of vaporization are "inert" from a gasdynamic point of view. At the right-hand limit of vaporization, the discontinuities in the velocity of sound are on the order of 1 m/sec. The discontinuities of the volumetric velocity of sound at the limits of the melting curve are even less.

6. Refraction of Strong Shock Waves in Air

Following [1, 2], let us examine the question of the region of applicability of the law of a doubling of the mass velocity with splits.

The problem is posed analogously to [1, 2]. A graphical solution of the problem is shown in Fig. 4 (legend same as in Figs. 1 and 2; the numbers 1 and 2 relate to the adiabats of NaCl and air, respectively), and the results are given in Fig. 5 (the solid line relates to NaCl, the dashed line to granite, and the dashed-dot line to $u_{gr} = 0.5u_{sur}$; the number 1 denotes the region of partial melting). The connection between the velocity of a split-off u_{sur} and the mass velocity in the arriving wave u_{gr} is represented by the following approximate dependences:

$$u_{gr} = \begin{cases} 0.5\,u_{sur} & \text{for } u_{gr} \leqslant 1.88, \\ 0.39 + 0.396\,u_{sur} & \text{for } u_{gr} \geqslant 1.88, \end{cases}$$

where u is in km/sec.

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DYNAMIC STRESS CONCENTRATION IN GLASS-FIBER-REINFORCED PLASTIC

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INTRODUCTION

In this paper the problem of stress concentration around defects is investigated. The discrete model of glass-fiber-reinforced plastic [1, 2] is used, in which it is assumed that the fibers work on expansion and the bonding on shear; the inertia of both components is taken into consideration.

§1. Let the glass-fiber-reinforced plastic consist of an infinite number of fibers of width h with their number indicated by integers j. The fibers alternate with layers of the bonding of width H. The y axis is parallel and x axis perpendicular to the fibers. The displacement of the bonding along the y axis is denoted by $v_j(x, y, t)$; the index j shows that the point under investigation lies between the j-th and (j + 1)st fibers at a distance x from the j-th ($0 \leqslant x \leqslant H$); t is the time. The displacement of the fiber is denoted by $u_j(y, t)$. Hooke's law has the following form:

$$\sigma_j(y, t) = \mathrm{E}\,\partial u_j(y, t)/\partial y,\ \tau_j(x, y, t) = G\,\partial v_j(x, y, t)/\partial x, \tag{1.1}$$

where σ_j and E are the normal stress and the Young modulus in the fiber and τ_j and G are the tangential stress and the shear modulus in the bonding.

It is shown in [2] that for zero initial conditions the behavior of the above system is described by the equations

$$\begin{gathered}\omega^2 \frac{d^2 u_j^L}{dy^2} + \beta^2 \left(u_{j-1}^L - \alpha u_j^L + u_{j+1}^L\right) = 0,\\ \beta^2 = G/\mathrm{E},\ \omega^2 = Hh\,\mathrm{sh}\,\lambda/\lambda,\ \lambda = pH/c_2,\\ \alpha = p^2\omega^2/\beta^2 c_1^2 + 2\,\mathrm{ch}\,\lambda,\quad c_1^2 = \mathrm{E}/\rho_1,\ c_2^2 = G/\rho_2,\end{gathered} \tag{1.2}$$

where the index L denotes the Laplace (time) transform of the desired quantities, p is the transform parameter, and ρ_1 and ρ_2 are the densities of the fiber and bonding materials, respectively. After determining u_j^L, the displacement in the bonding is determined by the formula

$$v_j^L = \left[u_j^L(y, p)\,\mathrm{sh}(\lambda - \lambda x/H) + u_{j+1}^L(y, p)\,\mathrm{sh}(\lambda x/H)\right]/\mathrm{sh}\,\lambda, \tag{1.3}$$

and the stresses σ_j^L and τ_j^L are determined in accordance with (1.1) and (1.3). The solution of (1.2) that vanishes at $y \to \infty$ has the form [2]

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