Self-consistent Equation of State for water behind strong shock wave

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Abstract

A generalization of the virial theorem for the variable, with dependence from temperature and density, degree of potential energy uniformity is obtained. On the ground of the first principles a closed analytical description of the internal potential energy, which is an exact solution of the nonlinear Riemann-Hopf equation is stated. The explicit analytical self-consistent wide-range equation of state for an arbitrary condensed medium is established. The Mi-Gruneisen complete self-consistent analytical form of the equation of state (EOS) for water behind a strong shock front is also obtained. The dependence of the exponent of the Tait–Murnaghan isothermal EOS of water on the intermolecular force and Gruneisen’s parameter is obtained. The correctness for the solution of closure problem for the hydrodynamics equations of the compressible media by using the equation of state is considered.

1. Introduction

To solve fundamental and applied problems of high pressure and temperature physics, as well as problems of hydrodynamics, plasma physics and astrophysics, the equation of state (EOS) of the medium is used [1]-[17]. The EOS, which is usually a functional relationship of pressure with density and temperature, is used as an additional equation that makes it possible to make a closed system of equations of hydrodynamics of a compressible medium [2]-[4]. EOS is interest also by itself, giving a description of stationary, equilibrium and locally equilibrium states of matter [1], [5], [6]. In particular, the EOS applies to study of the extreme states of matter at ultrahigh pressures and temperatures characteristic of the inner regions of planets and other space objects, as well as for energy technical systems [16]. The use of the EOS gives certain advantages in comparison with numerical methods of molecular dynamics, naturally complementing them when analyzing the states of the medium taking into account the interaction of particles [4]-[6].
Due to the absence of a small parameter characterizing the strong interaction of the particles of the medium at its extreme states, the problem of obtaining an analytical EOS based only on the first principles remains unsolved until now. The existing methods for obtaining the EOS using virial decompositions by degrees of density are based on the numerical determination of the type of fitting functions of temperature for the corresponding decomposition coefficients [3], [5], [6]. Similarly, in [2], [3] it is necessary to use additional data from experimental observations of shock wave parameters to reconstruct the EOS based on the integral form of the equations of hydrodynamics of a compressible medium in the form of Rankine-Hugonio relations.

As a result, well-known approaches to determining the EOS, including its tabular form [14], also leave open a number of problems of the hydrodynamics of a compressible medium, where the use of an analytical explicit form of the EOS is required [8]-[13]. Up to now it is difficult to separate the influence of the non-ideal behavior in the thermodynamic functions in the interpretation of the existing experimental data due to the various theoretical assumptions that are introduced besides first principles.

For example, in [17] a wide-range analytical EOS for water in the Mi-Gruneisen type is considered (see also [15]). This EOS can be applied at pressures up to $4 \times 10^{12}$ Pa, which, for example, corresponds to the problem of fusion ignition, considered in [16]. In this EOS, the total pressure $p = p_\rho(\rho) + p_T(\rho;T)$ and the total internal energy (per unit mass) $u = u_\rho(\rho) + u_T(\rho;T)$ are described as the sum of thermal and mechanical components of the energy. Where $\rho = mN/V; u = E/Nm$ and $N$ is the number of particles of a mass $m$ in a volume $V$. Here $p_\rho = T^2u_\rho / d\rho$ and for the Mi-Gruneisen EOS the relation $p_T = \rho \Gamma_T u_T$ is suggested, where in the common case the Gruneisen coefficient $\Gamma_T(T;\rho)$ determines the relation between the thermal part of the pressure and the thermal part of the internal energy $u_T$.

At the same time, [17] uses a well-known thermodynamic relation in the form

$$\rho^2\left(\frac{\partial u}{\partial \rho}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

(see (16.5) and (16.3) in [1] and (15) in [17]), which directly follows from the first law of thermodynamics and gives a connection between the thermal part of internal energy and the thermal part of pressure.

However, a closed analytical EOS in this approach can be obtained only in the case of an incomplete form of the EOS, when an additional assumption is made that the Gruneisen coefficient $\Gamma_T$ does not depend on temperature [15].

Indeed, there are only two equations for three unknown functions функций $\Gamma_T(T;\rho); p_T(T;\rho)$ and $u_T(T;\rho)$, which does not allow a closed description of these three functions. As a result, it is necessary to attract additional data obtained from the experiment on the value of the isochoric heat capacity, through which all other thermodynamic functions are expressed [17], [15].
In this paper, a closed analytical description based on the use of an additional equation corresponding to the well-known virial theorem [1] is obtained for these unknown three functions. Thus, from the first principles the complete Mi-Gruneisen equation of state by taking into account the dependence of the Gruneisen coefficient on temperature is obtained.

The significance of the virial theorem is that it allows the average kinetic and potential energy to be calculated even for very complicated systems and holds even for systems that are not in thermal equilibrium [1], [19], [20]. The well-known van der Waals EOS was obtained as a first application of the virial theorem [20]. Virial theorem also was used in [21] to obtain an analytical form of the EOS for water and steam near the critical point. An analytical relationship between pressure, specific volume and temperature were received in [21], based on the virial theorem in the form of a statistical integral depending on the type of potential of intermolecular interaction (see also [5], [6]). However, despite the successful application of this EOS near the critical point, this approach does not offer an explicit analytical form of EOS in the form of Mi-Gruneisen to describe the parameters of strongly compressed water behind the shockwave front. Indeed, using the EOS (see equation (23) in [21]), one cannot obtain an explicit analytical form for the energy density and the Gruneisen coefficient. This is because in general case, the potential energy of the intermolecular interaction must be expressed in terms of macroscopically measured parameters of the medium.

The latter can be done using the virial theorem with the assumption of uniformity of the function, describing the potential of intermolecular interaction or by use of the similarity analyses as it is provided in [22] to obtain the EOS based on the generalized Fermi-Thomas theory.

In [22], however, the consideration is limited only to the case of the Coulomb interaction potential proportional \( O(1/r) \), as required when formulating the boundary condition in the limit
\( r \to 0 \) for the Thomas-Fermi model. In contrast to metals, when considering the interaction of charged particles in a dielectric, it is already possible to have exponents that do not coincide with the monopole Coulomb potential for the corresponding interaction potential. In this case, the potential energy of the interaction can already be proportional to \( r^{-\tilde{d}} \) in the limit \( r \to 0 \), when the dependence of the exponent \( \tilde{d} = \tilde{d}(r) \) on the distance to the point source of the field appears. This is analogous to the introduction of the dependence of the charge magnitude on the distance due to the polarization of the vacuum, considered as an analog of the dielectric medium [23]. At the same time, the case when \( \tilde{d}(r) \to 0 \) in the limit \( r \to 0 \), is also similar to the effect of asymptotic freedom [24].

In this regard, here in Appendix A, a generalization of the consideration of the method of scale and charge similarity of work [22] for the specified more general type of interaction potential is proposed and the conclusion of the virial theorem for the case \( \tilde{d} \neq \text{const} \) is obtained. At the same time, it is shown that the index of uniformity \( d = \tilde{d} + d(\tilde{d}(q)) \) \( dq,q = \ln(\ln r) \) of potential energy no longer coincides with the value of the exponent \( \tilde{d} \) in the case when \( \tilde{d} \neq \text{const} \) and can weakly (logarithmically) depend on the temperature and density of the medium.

In this case, one can express the average potential energy of the system in terms of its macroscopic parameters (pressure, density and temperature) by using the virial theorem and the first law of thermodynamics and so one can obtain self-consistent EOS for water or any other condensed matter.

In paragraph 2, based on the virial theorem and the first law of thermodynamics, a closed description for potential energy is obtained in the form of an exact analytical solution of the nonlinear Riemann-Hopf type equation which corresponds to the complete analytical EOS for
any condensed medium. In Section 3, an analytical form for the Gruneisen coefficient and internal energy, which allows to a self-consistent description of the EOS of water under strong compressions is obtained. In Section 4, the dependence of the isothermal EOS exponent for water on the Gruneisen parameter and on the exponent of potential interaction between water molecules for different compression is shown. The discussion is provided in Section 5.

2. Analytical EOS for the condensed matter

Let us consider a finite non-periodic system of \( N \) particles, each of mass \( m \) that confined to a volume \( V = mN / \rho \) when the internal potential energy \( E_p(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) / mN = u_p \) is determined by interaction between particles with potential of force which is proportional to \( r^{-\tilde{d}(r)} \). In Appendix A, based on the use of the similarity method developed in [22], but for the case of functional dependence of the exponent \( \tilde{d} \) the ratio between the kinetic and potential energy of the system in the form of virial theorem is obtained. Indeed, in the case of a variable value of the exponent \( \tilde{d} \), there is also a relation \( \sum_{i=1}^{N} \vec{r}_i \cdot \frac{\partial u_p}{\partial \vec{r}_i} = -du_p \) for locally homogeneous functions \( u_p \), for which the relation \( u_p(\lambda \vec{r}_1; \ldots; \lambda \vec{r}_N) = \lambda^{-d} u_p(\vec{r}_1; \ldots; \vec{r}_N) \) is fulfilled only in the case \( \lambda - 1 \ll 1 \). This gives the generalization of Euler's theorem, which was considered earlier only in the case of globally homogeneous functions with a constant value of the exponent \( \tilde{d} = const \).

The value of the potential energy homogeneity index is generally represented as (see Appendix A):

\[
\tilde{d} = \tilde{d}(r) + r \ln r \frac{d}{dr} \tilde{d}(r)
\] (1)
Thus, the virial theorem, at an arbitrary form of dependence $\tilde{d}$ on $r$, includes a value $d$, that is associated with $\tilde{d}$ by the relation (1).

Let us look for a solution for the potential energy in the form $u_p/u_0 = (\rho/\rho_0)^{d(\rho; T)/3}$ where it is taken into account that the average distance between the particles of the medium is proportional to the value $r/r_0 = (\rho/\rho_0)^{-1/3}$ (see also (3) in [25]).

At this step, the function $d(\rho; T)$ is still an unknown function of temperature and density, which is convenient for further consideration, on the contrary, to represent as a function of the potential energy and density of the medium in the form:

$$d = \frac{3\ln(u_p/u_0)}{\ln(\rho/\rho_0)}$$  \hspace{1cm} (2)

At the same time, unlike the well-known virial method of decompositions [4]-[6] by integer degrees of density, the form of the function $d(\rho; T)$ is determined further without any additional assumptions and only from a closed self-consistent system of equations, which reduces to the solution of the Riemann equation.

Taking into account (2) and the well-known representation of the virial theorem [1], we obtain a representation for pressure (see also Appendix A):

$$p = \frac{kT}{m} \rho + \rho d(\rho; u_p)u_p/3 = \frac{kT}{m} \rho + \rho u_p \ln(u_p/u_{p0}^*/\ln(\rho/\rho_0^*))$$ \hspace{1cm} (3)

Let us use the definition of density (per unit mass) full of energy $u = E/mN = (E_K + E_p)/mN$ in the form:
From the first law of thermodynamics follows an equation supplementing equation (3), and having the form [1]:

\[
T \left( \frac{\partial p}{\partial T} \right)_\rho - p = -\rho^2 \left( \frac{\partial u}{\partial \rho} \right)_T
\]  

(5)

After substituting representations (3), (4) in (5) and introducing new variables, we obtain a Riemann type equation [26], [27], which describes the dependence of the potential energy density on density and temperature:

\[
\frac{\partial w}{\partial \tilde{y}} + (w + 1) \frac{\partial w}{\partial x} - w = 0; \quad w = \ln(u_p / u_{p0}); \quad \tilde{y} = \ln \ln(\rho / \rho_0); \quad x = \ln(T/T_0)
\]  

(6)

In (6), for the introduction of a dimensionless unknown function \( w \) and variables \( x, \tilde{y} \), the corresponding arbitrary constant values are introduced, the values of which must be determined by taking into account the boundary or initial conditions.

Using the Lagrange-Sharpie method, we obtain a general implicit solution of equation (6) in the form of a transcendental algebraic equation for the function \( w \):

\[
a(w + 1) + (a + 1) \ln w = b + ax + \tilde{y};
\]

\[
a = \frac{\partial w / \partial x}{\partial w / \partial \tilde{y}} = \frac{w_0 / w_0^\gamma - 1}{w_0 + 1} = \text{const}; \quad w_0^\gamma = \left( \frac{\partial w}{\partial \tilde{y}} \right)_{x=x_0; y=y_0}
\]

\[
b = a(w_0 + 1) + (a + 1) \ln w_0 - ax_0 - \tilde{y}_0 = \text{const}; \quad w_0 = w(x = x_0, \tilde{y} = \tilde{y}_0)
\]  

(7)
In order to make sure that the solution (7) exactly satisfies equation (6), it is enough to substitute in (6) representations for derivatives $\partial w/\partial x; \partial w/\partial \tilde{y}$ that are obtained from (7) directly by differentiating (7) with respect to the corresponding variables:

$$\frac{\partial w}{\partial x} = \frac{aw}{a(w+1)+1};$$
$$\frac{\partial w}{\partial \tilde{y}} = \frac{w}{a(w+1)+1}$$

(8)

In this case, the representations for the two integration constants given in (7) are obtained taking into account the solution given in (7) and (8).

For comparison, we also give the solution of equation (6) in the limit $w \gg 1$, when equation (6) has the form:

$$\frac{\partial w}{\partial \tilde{y}} + w \frac{\partial w}{\partial x} - w = 0$$

(9)

The exact analytical implicit the solution of equation (9) has the form:

$$a(w+1) + \ln(w+1) = b_1 + ax + \tilde{y}$$

(10)

$$\frac{\partial w}{\partial \tilde{y}} = \frac{w+1}{a(w+1)+1}; \frac{\partial w}{\partial x} = \frac{a(w+1)}{a(w+1)+1}$$

(11)

$$b_1 = a(w_0 + 1) + \ln(w_0 + 1) - ax_0 - \tilde{y}_0 = const;$$

$$a = \left( \frac{\partial w}{\partial \tilde{y}} \right)^{-1} \bigg|_{x=x_0; \tilde{y} = \tilde{y}_0} \frac{1}{w_0 + 1}$$

(12)

Note that the nonlinear equation (9), in contrast to the case of the nonlinear equation (6), admits not only an implicit form of the solution in the form of a transcendental equation (10), but also an explicit analytical general solution, which is given further in (16). At the same time,
however, the question remains whether this explicit general solution admits, as a special case, an exact solution of the transcendental equation (10). It is further shown that the solution obtained by the Lagrange-Sharpie method for the case of a linear equation, in fact, can be a special case of the general solution of this linear equation.

To do this, consider the limit \( w << 1 \) corresponding to the limit \( d << 1 \) of weak interaction between particles at a fixed density value, since, according to Eq. (1) and Eq. (2), there is a limit. In this limit, Eq. (6) becomes a linear equation and has the form:

\[
\frac{\partial w}{\partial y} + \frac{\partial w}{\partial x} - w = 0
\]  

(13)

Indeed, the Lagrange-Sharpie method leads to the following type of solution (13), which is also directly obtained from solution (7) in the limit \( w << 1 \):

\[
w = C \exp \left( axle + \frac{y}{a+1} \right) ; a = - \frac{w_{0r}'}{w_{0r} - \frac{w_0}{T_0}} = \text{const} ;
\]

\[
w_0 = w(x = 0; \tilde{y} = 0) ; w_{0r}' = \left( \frac{\partial w}{\partial T} \right)_{x=0; \tilde{y}=0}
\]  

(14)

\[
C = \exp \left( \frac{b-a}{a+1} \right) = w_0 = \text{const}
\]

The solution (14) of equation (13) depends on two arbitrary constants \( C; a \). On the other hand, the general solution of equation (13) can be obtained up to an arbitrary function, since it is a partial differential equation of the first order:

\[
w = e^{\tilde{y}} F_0(x - \tilde{y})
\]  

(15)
In Eq. (15) $F_0$ is an arbitrary smooth function and in the case $F_0(x - \bar{y}) = C \exp\left(\frac{a(x - \bar{y})}{a+1}\right)$ the solution (14) is a special case of the general solution (15).

Equation (9), obtained from (6) in the limit $w \gg 1$ and having an implicit solution (10), exactly coincides with the modification of the Riemann-Hopf equation considered in [26], [27], where its exact solution is obtained.

Thus, in addition to the implicit solution in the form (10), a general [its exact explicit analytical solution of equation (9) having the form [26], [27] is known:

$$w(x; y) = y \int_{-\infty}^{\infty} d\xi \bar{w}_0(\xi) \left(1 + y \frac{d\bar{w}_0}{d\xi}\right) \delta(\xi - x + y\bar{w}_0(\xi)); y = \exp \bar{y} = \ln \frac{\rho}{\rho_0} \quad (16)$$

In (16), the Dirac delta function is used under the integral, and the solution itself is obtained using the representation $w(x; y) = y\bar{w}(x; y); \bar{w}_0(x) \equiv w(x; y = 0)$.

Based on solution (16), we obtain the following explicit exact solution for the exponent of the potential energy:

$$d(\rho; T) = \int_{-\infty}^{\infty} d\xi d_0(\xi) \left(1 + \ln(\rho/\rho_0) \frac{d}{3d\xi}(d_0(\xi))\right) \delta\left(\xi - \ln(T/T_0) + \frac{d_0(\xi)}{3\ln(\rho/\rho_0)}\right); \quad d_0 = 3\bar{w}_0; d(\rho = \rho_0; T) \equiv d_0(\ln(T/T_0)) \quad (17)$$

At the same time, with respect to the behavior of the function $d_0(\ln T/T_0)$ in the limit of large values of the argument, the condition assumes its fairly rapid tendency to zero. Such a condition is necessary for the convergence, for example, of the integral of the square of the temperature derivative for the solution (17).

Taking into account (17) the equation of state (3), (4) has the form:
The form of the function $d(\rho; T)$ in Eq. (18) is defined in solution (17). From (17) follows a relatively weak logarithmic dependence of the exponent of the degree of potential energy on density and temperature. With relatively small compressions $\varepsilon = \frac{1}{3} \ln \left( \frac{\rho}{\rho_0} \right) \ll 1$, when (17), taking into account the properties of the delta-function follows the representation:

$$
\begin{align*}
    d(\varepsilon; x) &= d_0(T) \left[ 1 - \varepsilon \frac{d}{dx} (d_0) + 2\varepsilon^2 \left( 2 \left( \frac{d}{dx} d_0 \right)^2 + d_0 \left( \frac{d^2}{dx^2} d_0 \right) \right) + O(\varepsilon^3) \right]; \\
    x &= \ln \frac{T}{T_0}; \varepsilon = \frac{1}{3} \ln \frac{\rho}{\rho_0}
\end{align*}
$$

(19)

Note also that for finite values of the parameter $\varepsilon = \varepsilon(\rho)$, the function (17) in the case $\frac{d}{dT} d_0 < 0$ can maintain smoothness only under the condition [26], [27]:

$$
\frac{1}{3} \ln \left( \frac{\rho}{\rho_0} \right) \equiv \varepsilon < \varepsilon_{th} = \frac{1}{\max_T \left( T \left| \frac{d}{dT} d_0(T) \right| \right)}
$$

(20)

Condition (20) is similar to the criterion for the existence of a smooth solution of the Riemann equation only on a finite time interval, when the analogue of the time variable is a parameter $\varepsilon$ determined by the amount of compression of the medium. If condition (20) is violated, the value of the square of the derivative of the temperature function (17) already has a singular behavior depending on the compression value. In fact, this may be an analogue of a phase transition of the
second kind, when the discontinuity takes place not for the thermodynamic functions themselves, but for their derivatives. Indeed, it follows from (17) that for the case \( \frac{d}{dT}d_0(T) < 0 \) only under condition (20) the convergence of the integral having the form [26], [27] is ensured:

\[
\int_{-\infty}^{\infty} dx \left( \frac{\partial}{\partial x} d(x; \varepsilon) \right)^2 = \int_{-\infty}^{\infty} dx \frac{\left( \frac{d}{dx}d_0(x) \right)^2}{1 + \varepsilon \frac{d}{dx}d_0(x)} < \infty \quad (21)
\]

Let us establish a correspondence between the function \( d_0(T) \) and the dependence of pressure on temperature at a fixed density. To do this, we use the representation for the pressure in (18) in the limit \( \rho \to \rho_0 \). At the same time, from (18) we obtain:

\[
d_0(\ln(T/T_0)) = \frac{3}{u_0} \left( \frac{p(\rho = \rho_0; T) - kT}{\rho_0} \right)
\]

To find the dependence of pressure on temperature for a given density value, one can use the known temperature dependence for the coefficient \( \alpha(T; \rho) = \left( \frac{\partial \ln p}{\partial T} \right)_{\rho=\text{const}} \) (see Fig. 1):

Fig. 1 The dependence of the coefficient \( \alpha = \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_{\rho=\text{const}} \) on the temperature [39].
The equation of state obtained in (18) can be used taking into account (17), both for the case of an exact analytical solution having an implicit form in (7), and for limiting cases \( w < < 1 \) and \( w >> 1 \), when there are already explicit analytical solutions for potential energy in the form of (14) and (16), respectively.

As a result, without any additional assumptions, based only on the first principles used to obtain the equation of state (18) (taking into account (7), (14), (16)), it is also possible to obtain analytical representations for such important thermodynamic quantities as the specific isochoric heat capacity \( c_v = \left( \frac{\partial u}{\partial T} \right)_\rho \), specific isobaric heat capacity \( c_p = \left( \frac{\partial (u + p/\rho)}{\partial T} \right)_\rho \), isothermal compressibility \( \beta_T = 1/\rho c_v^2 \), \( c_T^2 = \left( \frac{\partial p}{\partial \rho} \right)_T \) and the thermal expansion coefficient \( \alpha_p = \beta_T \left( \frac{\partial p}{\partial T} \right)_\rho \).

In this case, for example, the Boyle temperature \( T = T_B \), can be set at which the second virial coefficient \( B = \lim_{\rho \to 0} \left( \frac{\partial (pm/kt\rho)}{\partial \rho} \right) \) vanishes (at the same time \( B > 0 \) for values \( T > T_B \)), as well as the temperature \( T = T_{max} \) at which this coefficient reaches the maximum value, as a function of temperature \( (\partial B/\partial T)_{\rho} = 0; (\partial^2 B/\partial T^2)_{\rho} < 0 \) [5], [6]. The physical meaning of the Boyle temperature corresponds to the temperature at which the forces of attraction and repulsion between the particles balance each other and the particles behave as in an ideal gas without interacting with each other, or when \( d \propto \tilde{d} \to 0 \) by analogy with asymptotic freedom [24].

Therefore, we use the equation of state following from (3) and (14) (or (18) and (14)), obtained precisely in the limit \( d \propto w << 1 \), to estimate a value that has the form:
\[
B = \frac{u_p m C}{kT} \lim_{\rho \to 0} \frac{\exp(F + F_1)}{(1 + a) \rho \ln^2 \rho / \rho_0} \left[ -a + C \exp F \right], \\
F = \frac{a \ln T / T_0 + \ln \rho / \rho_0}{a + 1}; F_1 = C \exp F 
\]

(23)

At the same time, it follows \( B = 0 \) from (23) that when the square bracket in (23) is zeroed. This gives an estimate for the Boyle temperature in the form:

\[
T_B / T_0 = (a / C)^{a+1} (\ln \rho / \rho_0)^{-1/a} 
\]

(24)

Indeed, it follows that \( B > 0 \) in (23) at a temperature of \( T > T_B \) when \( T_B \) is obtained from (24). The Boyle temperature in (24) has a weak logarithmic dependence on the density for any finite density values. However, in the limit of arbitrarily small density, the Boyle temperature tends to zero at \( a > 0 \), but at negative values \( a < 0 \) in this limit, the Boyle temperature tends to infinity. This is consistent with the condition of the function \( d_0(\ln T / T_0) \) vanishing on the limits of integration in (17) within \( T \to 0 \) and \( T \to \infty \). In addition, there is no finite value of the second virial coefficient in the zero-density limit for solution (23) due to the presence of a dependence on the density of the multiplier with a square bracket in (23). This indicates that only under limited conditions for the density value, it is possible to carry out a correct virial decomposition by degrees of density for pressure when corrections to the equation of state of an ideal gas are obtained, taking into account the interaction of particles. Such conditions, apparently, were not taken into account earlier [1]. Similarly, from (23) for the temperature \( T = T_{max} \) at which the first derivative vanishes \( (\partial B / \partial T)_\rho = 0 \), we obtain the representation:
\[
T_{\text{max}}^\pm = \left( \ln \frac{\rho}{\rho_0} \right)^{-1/a} \left[ \frac{a^2 + 1 - a \pm \sqrt{(a^2 + 1 - a)^2 - 4a^2}}{2aC} \right]^{a+1};
\]

where \( a \geq a_\pm = \frac{3 + \sqrt{5}}{2} \approx 2.618033 \) or \( a \leq a_- = \frac{3 - \sqrt{5}}{2} \approx 0.381966 \)

In (25) there are restrictions on the parameter \( a \), under which the root expression in (25) is not negative. In this case, in particular, for the case \( a > a_\pm \) in (25), the inequality \((\partial^2 B / \partial T^2)_\rho < 0\) and, accordingly, the maximum of the function \( B \) at temperature (25) take place at two different temperature values \( T = T_{\text{max}}^+ \). On the other hand, under the condition \(-1 < a \leq a_\rho \approx 0.275 < a_- \) in (25) there is only one maximum value of the function \( B \) already at only one value of the temperature \( T = T_{\text{max}}^- \), defined in (25). For all cases when the constraint in the form \( a < -1 \), is fulfilled, the function \( B \) has again two maxima, which are reached at two different temperatures \( T = T_{\text{max}}^\pm \). However, it turns out that if we consider for solutions (24) and (25) the known condition \( T_{\text{max}} > T_B \) [5], [6], then in (25) there remains only one solution \( T_{\text{max}} = T_{\text{max}}^+ \), for which the specified necessary condition is satisfied for any values \( a < a_- \).

A more detailed study is carried out later in the Discussion section, and a comparison with the results obtained from empirical equations of state and calculations by the method of molecular dynamics can also be considered separately. [5], [6], [28], [29].

At the same time, it follows from the solutions obtained above that the uniformity index of the function characterizing potential energy has a very weak logarithmic dependence on temperature and an even weaker doubly logarithmic dependence on density. This circumstance allows us to consider an approximation in which, at significant finite intervals of temperature and compression, a characteristic constant value of this parameter \( d \), corresponding to these intervals
can be used by analogy with the exponent of the isothermal equation of state of water of the Taita-Muranheim type [2]. In the next paragraph, such an approximation is used to obtain the complete Mi-Gruneisen equation of state.

3. The Mi-Gruneisen EOS

The Gruneisen coefficient in the Mi-Grunaisen EOS should be distinguished from the Gruneisen parameter \( \Gamma = \frac{1}{\rho} \left( \frac{\partial u}{\partial p} \right)_{\rho=\text{const}} = \frac{\beta}{c_v} \), which describes the compressibility of the medium and is a measure of thermal pressure, where \( \beta = -\frac{1}{\rho} \left( \frac{\partial p}{\partial T} \right)_{\rho=\text{const}} \) [30]. For an isothermal EOS of the Tait–Murnaghan type, the pressure and compression are \( p \propto \delta^n \) and \( \delta = \rho/\rho_0 \), where \( n = 2\Gamma + \frac{1}{3} \) relates the Gruneisen parameter \( \Gamma \) and the exponent \( n \) [31]. It was shown that, in the limit of high temperatures, the values of the Gruneisen parameter and the Gruneisen coefficient coincide [30]. For the special, not common EOS of the Mu-Gruneisen type when \( \partial c_v / \partial T = 0 \), they also coincide with each other \( \Gamma_T = \Gamma \).

Let us consider the common case when \( \Gamma_T = \Gamma (\rho; T) \neq \Gamma \). We use the suggestion about parameter \( d \approx \text{const} \) in (3), (4) and one obtains:

\[
    u = \frac{3 p}{d \rho} + \frac{kT}{m_{H_2} \rho} \left( \frac{1}{2} - \frac{1}{d} \right). \tag{26}
\]

Using Eq. (5) and the Gruneisen relation \( \rho_T = \rho \Gamma_T u_T \), one obtains

\[
    T \left( \frac{\partial (u_T \Gamma_T)}{\partial T} \right)_{\rho=\text{const}} = u_T \Gamma_T - \rho \left( \frac{\partial u_T}{\partial \rho} \right)_{T=\text{const}}. \tag{27}
\]

Here, \( p = p_\rho + p_T \) and the equality \( p_\rho = \rho^2 du_\rho / d\rho \) is used. Similarly, using Eq. (26), complementing Eq. (27), the equation for internal energy density can be obtained as
\begin{align}
\begin{align}
\frac{u_T - \frac{3}{|\mathbf{d}|} u_T \mathbf{f}^T}{u_T} = f(\rho) + A_T T \quad . \tag{28}
\end{align}
\end{align}
Here, \( f(\rho) = \frac{3 P}{d \rho} - u_\rho(\rho) \) and \( A_T = \frac{3k}{m_H} \left( \frac{1}{2} - \frac{1}{d} \right) \). The system of Eqs. (27) and (28) allows one to determine the EOS in the form of Mi-Gruneisen for an arbitrary medium. Let us note here that this approach assumes an isentropic or isothermal relation between the density and the temperature-independent part of the pressure. That is, in Eq. (28), the form of \( f(\rho) \) is assumed later to correspond to the isentropic EOS of water in the Tait–Murnagahan form (see below Eq. (30)) [2], [31]-[33].

Now, using function \( z(\rho ; T) = u_T \mathbf{f}^T \) and substituting this representation in Eq. (27), we obtain a partial differential equation:

\begin{align}
\frac{\partial z}{\partial x} + \frac{3}{d} \frac{\partial z}{\partial y} - z = -f_1(y) . \tag{29}
\end{align}

Here, \( x = \ln(T/T_0) \), \( y = \ln(\rho/\rho_0) \) and \( f_1(y) = df(\rho(y))/dy \). Let us consider the solution of Eq. (29) for the case when in Eq. (28) functions \( p_\rho(\rho) \) and \( f_1 \) have the forms

\begin{align}
p_\rho - p_0 = \frac{\rho_0 c_0^2}{n} (\delta^n - 1) ; \delta = \frac{\rho}{\rho_0} \\
f_1(y) = \frac{c_0^2}{n} \left( \frac{3(n-1)}{d} - 1 \right) \exp(y(n-1)) + \left( \frac{c_0^2}{n} \frac{p_0}{\rho_0} \right) \left( \frac{3}{d} + 1 \right) \exp(-y) . \tag{30}
\end{align}

Here, \( c_0^2 = \frac{\partial P}{\partial \rho} |_{T=T_0=\text{const}} \) is the square of the isothermal velocity of sound in undisturbed water and \( n \) is the dimensionless exponent, which in general depends on temperature and pressure. This dimensionless exponent is commonly assumed constant when considering a rather narrow range of pressure. For example, \( n \approx 7 \) is used for pressures \( \leq 25 \text{ kbar} \) in [2], [31]-[33].
For representations (18), the general solution of Eq. (17), has the form

\[ z(x; y) = e^{\frac{d}{3}x} \left( y - \frac{d}{3}x \right) - \frac{c_0^2}{n} e^{y(n-1)} + \left( \frac{c_0^2}{n} - \frac{p_0}{\rho_0} \right) e^{-y}. \]  

Here, \( F_0 \) is the arbitrary smooth function. Now, using representations (30) and Eq. (31), we obtain the EOS for water in the form of Mi-Gruneisen, i.e., \( p_T = \delta \rho_0 z(\delta ; T) \):

\[ p = p_\rho + p_T = \delta \frac{\rho_0 T}{T_0} F_0 \left( \ln \left( \frac{T_0}{T} \right)^{\frac{3}{2}} \right). \]  

Here, \( F_0(0) = \frac{p_0}{\rho_0} \) is the boundary condition and \( T_0 \) is the temperature of the undisturbed state of the medium characterized by the corresponding values of density \( \rho_0 \) and pressure \( p_0 \). Now, for the total internal energy density, using Eqs. (32) and (26), one obtains

\[ u = \frac{3kT}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{a} \right) + \frac{3T}{a \rho_0} F_0 \left( \ln \left( \frac{T_0}{T} \right)^{\frac{3}{2}} \right) \]

Eqs. (32) and (33) present the self-consistent EOS in the form of Mi-Gruneisen, where the pressure and internal energy density depend on the density and temperature. However, to find these dependencies, function \( F_0 \) should be determined. Here, it is assumed that the parameters \( n \) and \( |d| \) for each considered range of compressions and temperatures are constant values.

To determine the function \( F_0 \) we use the Rankin–Hugoniot relation as a second boundary condition, using the conservation energy law at the shock-wave (SW) front [2]:

\[ u - u_0 = \frac{1}{2} (p + p_0) \left( \frac{1}{\rho_0} - \frac{1}{\rho} \right). \]

By substituting Eqs. (32) and Eq. (33) in Eq. (34) one obtains
\[ \frac{T}{T_0} F_0 = \frac{2d}{6-d(d-1)} \left[ \frac{p_0}{\rho_0} \left( \frac{3}{d} + \frac{(\delta-1)}{2\delta} \right) - \frac{3k(T-T_0)}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) \right] \]  

(35)

Now, using Eqs. (28) and (31) and considering Eq. (32), we obtain explicit analytical representations for the thermal part of the internal energy density \( u_T \) and for the Gruneisen coefficient \( \Gamma_T \):

\[ u_T = u - u_p = \frac{6}{6-d(d-1)} \left[ \frac{p_0}{\rho_0} \left( \frac{3}{d} + \frac{(\delta-1)}{2\delta} \right) - \frac{3k(T-T_0)}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) \right] + A \]  

(36)

\[ \Gamma_T = \frac{z}{u_T}; z = \frac{T}{T_0} F_0 - \delta n^{-1} \frac{c_0^2}{n} + \delta^{-1} \left( \frac{c_0^2}{n} - \frac{p_0}{\rho_0} \right) \]  

(37)

Here, \( A = \frac{3kT}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) - u_p \) and \( u_p = \delta n^{-1} \frac{c_0^2}{n(n-1)} + \delta^{-1} \left( \frac{c_0^2}{n} - \frac{p_0}{\rho_0} \right) \).

From Eqs. (32) and (35) for the Hugoniot shock adiabatic, we obtain the following dependence of pressure \( p \) and internal energy density \( u \) on temperature and compression magnitude:

\[ p = \frac{2\rho_0 \delta d}{(d(d-1)-6)} \left[ \frac{3k(T-T_0)}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) - \frac{p_0}{\rho_0} \left( \frac{3}{d} + \frac{\delta^{-1}}{2\delta} \right) \right] \]  

(38)

\[ u = \frac{6}{(d(d-1)-6)} \left[ \frac{3k(T-T_0)}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) - \frac{p_0}{\rho_0} \left( \frac{3}{d} + \frac{\delta^{-1}}{2\delta} \right) \right] + \frac{3kT}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{d} \right) \]  

(39)

Note that for the case of a polytropic ideal medium with adiabatic index \( \gamma > 1 \) for a shock adiabatic, a dependence of the pressure similar to (38) was obtained (see (89.1) in [34]):

\[ \frac{p}{p_0} - 1 = \frac{\delta^{-1}}{(\gamma+1)/2\gamma - \delta(\gamma-1)/2\gamma}. \]

For the dependence of temperature on pressure and compression on the Hugoniot shock adiabatic (38), we use the following representation (see also below Fig.2):
\[
\frac{T}{T_0} = 1 + h \left( \frac{p}{p_0} \left( 6-d(\delta-1) \right) \right) \delta(2-d).
\] (40)

To obtain (40), the estimation \( h = \left( \frac{3kT_0\rho_0}{m_{H_2}\rho_0} \right)^{-1} \approx 0.000247 \) is used, where \( T_0 = 293K^0; c_0 = 1483 \frac{m}{s}; p_0 = 1\ bar; p^0/\rho_0 = 10^{-4}c_0^2/2.2, k = 1.38 \times 10^{-16} g \cdot cm^2/s^2 K^0; m_{H_2} = 3 \times 10^{-23} g \). In (40), for the values \( p, \delta \) and \( T \) it is necessary to use the values according to the data presented in Table 3 in [35] to obtain the values of \( |d| \) represented in Fig. 2.

Figure 2 shows the dependence of the temperature on pressure at various compressions and parameter \( d \) values in (40), which is obtained from Eq. (32) using Eq. (35). The comparison of this dependence with known data [14], [35], [36] is presented in Fig. 2. In [35], the shockwave and thermodynamic data pertaining to the Hugoniot curve are tabulated in Table III as a function of shock pressure. The specific volume, shock velocity, particle velocity, internal energy density, and enthalpy in this table were obtained from the analytical fit of the experimental Hugoniot curve data for water and from the Rankin–Hugoniot relations (see (1)-(3) in [34]). The SESAME tabular form of the EOS of water is given in [14], which allows one to determine the temperature value at a given pressure, compression, and internal energy density.

As a result, Fig. 2 shows the temperature-pressure dependence curve corresponding to the data in Table 3 of [35] and the parameter \( |d| \) values versus the pressure at which an exact correspondence between the data [35] and the equation (40) is realized. Figure 2 also shows the temperature-pressure dependence obtained using the SESAME EOS of water [14]. One can see a satisfactory correspondence between the curve following from the EOS for water near the shock adiabatic obtained in this paper and the tabular form of this SESAME EOS.
Fig. 2 The curve with black squares denotes the dependence of temperature on pressure, which corresponds to the exact solution (40), as well as to experimental data given in Table 3 [35], when using in (40) the values of the intermolecular interaction potential exponent $|d| = d > 0$ corresponding to the curve indicated by green triangles. For comparison, we present the dependence of temperature on pressure denoted by red circles obtained using the SESAME EOS of water [14].

The table below shows the values of the parameters corresponding to the data given in Fig. 2 [35] on the magnitude of pressure $p$, compression $\delta = \rho / \rho_0$, temperature $T$, as well as the velocity $D$ of the shock wave and the velocity $U$ of the medium behind the shock wave front in water.

| $p$(Kbar) | $\delta$ | $T^0$K | $D$(km/sec) | $U$(km/sec) | $d$ |
|-----------|-----------|---------|-------------|-------------|-----|
| $p_0 = 10^{-3}$ | 0.9982 | 293 | 1.483 | 0 | $\forall$ |
| 10 | 1.2189 | 327 | 2.352 | 0.426 | 36.411 |
| 20 | 1.3187 | 369 | 2.871 | 0.698 | 23.4968 |
| 40 | 1.4409 | 469 | 3.611 | 1.110 | 16.4868 |
| 60 | 1.5242 | 583 | 4.173 | 1.440 | 13.7223 |
| 100 | 1.6461 | 843 | 5.045 | 1.986 | 11.019 |
| 120 | 1.6969 | 983 | 5.404 | 2.225 | 10.1949 |
| 140 | 1.7422 | 1127 | 5.731 | 2.447 | 9.541 |
| 170 | 1.8057 | 1347 | 6.160 | 2.760 | 8.7413 |
The parameter \( d \) characterizes the paired effective interaction potentials. This coefficient becomes useful in the analysis of experimental data for strong shock wave propagation in water at pressures \( \geq 80 \) Kbar \[35\]. In this range of pressures, there is a simplification of molecular interactions, which is rather complicated at lower temperatures and pressures \[36\]. For example, the repulsive potential of the Lennard–Jones type with an exponent \( d = 12 \) is also considered in \[37\] in accordance with Fig. 2 for pressures \( > 60 \) Kbar.

Thus, the exact coincidence on Fig. 2 between the analytical equation of state \( (40) \) and the observational data from Table 3 \[35\] is established due to the appropriate choice of the only one fitting parameter \( d \). For example, at the pressure 80 kbar and temperature 600 K an exponent value is equal \( d = 12 \) in accordance with \[37\].

Using the exact solution \( (14) \), taking into account \( (2) \), we obtain the following analytical solution:

\[
d = \frac{3C}{\ln \delta} \exp \left( \frac{a \ln \frac{T}{T_0} + \ln \ln \delta}{a + 1} \right); \delta = \frac{\rho}{\rho_0}
\]  

(41)

Using the data given above in the table for the \( p = 60 \) Kbar and \( p = 100 \) Kbar from \( (41) \), it follows that for this pressure interval presented in Fig. 2 the dependence of the value \( d = d(\rho; T) \) corresponds to an approximation using solution \( (41) \) for the values of constants \( C \approx 24.87; a \approx -0.52 \) characterizing this solution. For comparison, in the pressure range from \( p = 100 \) Kbar to \( p = 120 \) Kbar, according to the table from \( (41) \), other values \( C \approx 15.55; a \approx -0.45 \) of constants already follow. This means that the approximation of the data
presented in Fig. 2 using solutions (14) and (41) is not universal and depends on the choice of the range of pressure and temperature changes.

In the limit $\delta^{n-1} >> 1$ of Eq. (37), the Gruneisen coefficient can be approximated as

$$\Gamma_T = n - 1.$$  \hfill (42)

Note that the relation between the exponent $n$ and the Gruneisen parameter $\Gamma$, obtained in [36], exactly coincides with (42). Thus, in this approximation the Gruneisen coefficient and the Gruneisen parameter are equal to each other $\Gamma_T = \Gamma$. The relation (42) is also known for the case of an ideal gas if the exponent $n$ coincides with the adiabatic exponent $n = \gamma$ [2]. Indeed, EOS (30) is similar to the EOS of an ideal polytropic medium [34], where the adiabatic index $\gamma = c_p/c_v$ plays a role similar to the exponent $n$ in (30).

In the limit $\delta \to 1 + 6/d$ at arbitrary temperatures (or in the limit of large temperatures at arbitrary compressions) using Eq. (37), the Gruneisen coefficient $\Gamma_T$ reads

$$\Gamma_T = \frac{d}{3}.$$  \hfill (43)

4. The Gruneisen parameter and the isothermal EOS

Let us consider an arbitrary value of $d$ as the fitting parameter in the relationship between the exponent $n$ in the EOS of water (30) and the Gruneisen parameter. In [38], the representation $n = \Gamma + 1$ is obtained. Let us note that in [38], the exponent $n$ is not dependent on the parameter $d$.

The Gruneisen parameter $\Gamma = \hat{c}_p^2\beta/c_v$ has the general form (see Appendix, the representations for $\hat{c}_p^2$ in (C9) and (C2) for $c_v$)
\[
\Gamma = \frac{d}{3 \left(1 + \frac{d k \delta^{-n+1}}{m_{H_2} c_0^2 \beta(T; p) \left(\frac{1}{d^2} - 1\right)}\right)} .
\] (44)

In this case, in (44), in particular, the representation (41) for the parameter \( d \) can be used, which corresponds to the exact analytical solution (14) according to the definition (2).

The function \( \beta = \beta(T; p) \) in (44) is shown in Fig. 3. As noted above, at sufficiently high temperatures, one obtains \( \Gamma_T = \Gamma \). From (44) in the limit \( \delta^{n-1} >> k/c_0^2 m_{H_2} \beta \), it follows that \( \Gamma \to d/3 \). The latter coincides with the estimate (42) for the Gruneisen coefficient.

For the case \( d \neq 2; \Gamma \neq \frac{d}{3} \) in (44) it is possible to obtain a relation of \( n \) with compression, temperature, and pressure (see Fig. 3 for the dependence of \( \beta(T; p) \) on pressure and temperature):

\[
n = 1 + \frac{1}{\ln \delta} \ln \left[ \frac{3 A_T \Gamma(d-2)}{2(d-3 \Gamma)} \right] .
\] (45)

Here, \( A_T = \frac{k}{m_{H_2} c_0^2 \beta(T; p)} \). In (45), an analytical dependence on compression and temperature can also be used for the parameter \( d \) from the exact solution (41).

---

![Graph](image-url)

Fig. 3. Dependence of the volume expansion coefficient \( \beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_{p=\text{const}} \) on temperature according to the known simulation data [39].
Let us apply Eq. (45) for a given compression value; the exponent of the potential of intermolecular interaction in water reads

\[ d = \frac{6\Gamma (1-A_T \delta^{-\frac{n-1}{2}})}{2-3A_T \Gamma \delta^{-\frac{n-1}{2}}} \]  

(46)

Now, using the data presented in [35] (see Table 3 in [35]) for the local sound velocity \( c_T \) at different compressions and Eq. (C9), one can calculate the values of \( n \) at different compressions.

Using the temperature dependence of the coefficient \( \beta(T) \) (see Fig. 3) and Eq. (32), the estimates of the modulus of the potential of intermolecular interaction \( d \) in water can be obtained. For example, for \( \delta \approx 1.318 \), according to [38] (see function \( \Gamma = \Gamma(\delta) \) in Fig. 11 in [38]) and [35] (\( c \approx 3390 \text{m/s}; c_0 \approx 1483 \text{m/s} \)) we estimate \( n \approx 6.9 ; \Gamma' \approx 0.9 \). For such compression, as follows from [35], the pressure is \( p \approx 20 \text{kbar} \) and the temperature is \( T = 96^\circ \text{C} \). In this case, the coefficient of thermal expansion is equal to \( \beta \approx 0.0008 \text{grad}^{-1} \) and \( A_T \approx 0.29 \). As a result, we estimate \(|d| \approx 2.76 \). Thus, according to (46), there is a non-monotonic dependence of \( d \) with increasing compression. However, according to (C9) for compression \( \delta \) and the square of the local speed of sound obtained from [35], there is a monotonous decrease in the exponent \( n \) versus the increase in compression in the isothermal EOS of water (30). On the other hand, for a fixed value of \( d \), a decrease in the Gruneisen parameter with an increase in compression from 1.6 to 2.3 may lead to a decrease in the value of \( n \) in the isothermal EOS of water (30).

5. Discussion of implications from the EOS
Thus, in this paper, a wide-range EOS of an arbitrary medium is obtained from the first principles, as well as a complete equation of state of water in the form of Mi-Gruneisen. The results obtained are important both in connection with the problem of closing the equations of hydrodynamics of a compressible medium and for understanding of the thermodynamic properties of pure fluids and there mixtures up to very high temperatures and pressures. For example, the last are required in geophysics and astrophysics because very few experimental $p - \rho - T$ data exist at these extreme conditions because water is thought to be one of the most abundant compounds in ice giants such as Neptune and Uranus [40]. Therefore EOS for water is critical to understanding there temperature and pressure distributions when the ANEOS, SESAME models [14], [41] and Quantum Molecular Dynamics (QMD) calculations [42] and QMD based EOS model [43] have been employed for modeling interior of ice giants as in the shock experiments [40].

The EOS known to date take into account the effects associated with the interaction of medium particles only in a certain limited range of changes in pressure, density and temperature [1], [2], [5], [6]. This limitation is due to a number of assumptions used in the derivation of the EOS. In this paper, a wide-range EOS of an arbitrary medium is obtained from the first principles, in which the interaction between the particles of the medium is taken into account without involving any additional assumptions. This makes it possible to assess the degree of adequacy of various approximations used to describe the medium when taking into account the interaction between the particles of the medium. For example, there is an idea of the applicability of the Tate-Muranheim type isothermal equation of state of water (30) with the value of the exponent $n = 7.15$ in the pressure range up to 25 Kbar [2], [31]-[33]. With an increase in compression with an increase in pressure, this indicator can change, however, remaining almost unchanged in
the corresponding limited ranges of pressure changes, as well as the associated exponent of the power-law for the interaction potential between particles. A similar refinement of the dependence on the pressure range can be carried out for parameters such as the Boyle temperature (see (24)) and the critical point \((T_c; \rho_c; p_c)\) determined from the conditions

\[
\left( \frac{\partial p}{\partial \rho} \right)_T = \left( \frac{\partial^2 p}{\partial \rho^2} \right)_T = 0 \quad [5], [6] \quad \text{based on the obtained analytical form of the EOS.}
\]

Here we limit ourselves to considering the exact analytical solution for the second virial coefficient, which is presented for the simplest case in the form (23).

Indeed, books on statistical mechanics have a chapter devoted to imperfect gases, in which the virial expansion of the EOS in terms of density is derived [1] (see also in [44]). Explicit evaluation of the second virial coefficient is given only in simple cases as hard spheres and square well potentials and a simple analytical closed form is also obtained in [44], which is especially useful at low temperatures where the series expansion of virial coefficient converges very slowly. At the same time, to estimate the second virial coefficient in [44], an alternative definition was used to the one given and used in (23), which has the form

\[
\tilde{B}(T) = -\frac{2\pi}{3kT_0} \int dr \frac{du}{dr} \exp \left( -\frac{u}{kT} \right) \quad \text{for the case of the Lennard-Jones potential}
\]

\[
u = u_{LD} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],
\]

describing the interaction between the particles of the medium depending on the distance between the particles \(r\). This definition of the second virial coefficient is considered as equivalent to the definition used in (23), which is based on the use of the equation of state of the medium relating pressure, density, temperature [5], [6].
In particular, in [44], after the introduction of dimensionless variables

\[ B'(T^*) = \tilde{B} / (2\pi \sigma^3 / 3) \]

\[ T^* = kT / \varepsilon \]

the following estimates were obtained for the Boyle temperature \( T^*_B \approx 3.417927 \) at which \( B'(T^*_B) = 0 \) as well as the temperature \( T^*_\text{max} \approx 25.15257 \) at which the second virial coefficient reaches the maximum value \( (dB^*/dT^*)_{T^*-T^*_\text{max}} = 0 \). We may consider these estimates on the basis of an exact analytical solution for the corresponding quantities (24) and (25), assuming that the equality \( T/T_0 = T^* \) in (24) and (25) is fulfilled.

In particular, as in [44], from (24) and (25) follows the fulfillment of the necessary ratio

\[ T^*_\text{max} > T^*_B, \]

which can take place only if \( a < a_\approx 0.381 \) when one branch of the solution

\[ T^*_\text{max} = T^*_\text{max}^+ \]

is selected in (25). As shown above, the data in Fig.2 are consistent with the solution (14), (41) and, respectively, with the representations (23)-(25) for the second virial coefficient and temperatures \( T^*_B, T^*_\text{max}^+ \) for the values \( a \approx -0.52 \) and \( a \approx -0.45 \). Both of these values satisfy the condition \( a < a_\approx 0.381 \) under which the relation \( T^*_\text{max}^+ > T^*_B \) is fulfilled.

We shall also focus on the question of using the EOS of a compressible medium to close the equations of hydrodynamics of such a medium.

Indeed, even when describing obviously non-equilibrium macroscopic processes using the equations of hydrodynamics of a compressible medium, the EOS is used to obtain a closed description of the system under the assumption of the realization of local thermodynamic equilibrium [45], [2], [3]. L. Euler was the first who noted such a necessity of using the equation connecting pressure and density to close the hydrodynamic description in the case of consideration of the dynamics of a compressible medium [45]: “Let us now turn to those elements which contain that which is unknown. In order to properly understand the motion that will be imparted
to the fluid it is necessary to determine, for each instant and for each point, both the motion and the pressure of the fluid situated there. And if the fluid is compressible, it is also necessary to determine the density, knowing the above-mentioned other property which, together with the density, makes it possible to determine the elasticity. The latter, being counterbalanced by the fluid pressure, must be considered equal to that pressure, exactly as in the case of equilibrium, where I have developed these ideas more thoroughly”. Thus, L. Euler introduced a qualitative difference between the pressure included in the equation of state of the medium, which he called elasticity and dynamic pressure, the gradient of which is included in the Euler equation, although at the same time an assumption was made about the possibility of quantitative identification of these quantities, like in the case of the medium is in an equilibrium state [45].

How to justify such an assumption is the subject of further consideration. Indeed, even in the case of a relatively weak disturbance of the equilibrium state in the presence of medium flows at speeds much lower than the speed of sound, when the incompressible medium approximation is valid, there is a dependence of the dynamic pressure on the gradients of the medium velocity. In this case, the closure of the hydrodynamic equations dispenses with the use of the EOS of the medium. Therefore, it does not seem quite consistent when, for obviously non-equilibrium near sonic and supersonic flows, the pressure is set only on the basis of an EOS that does not contain velocity gradients of a compressible medium in any explicit form generalizing the case of an incompressible medium. In this regard, in [46]-[48] various variants of the closure of the equations of hydrodynamics are considered in cases where it is possible to exclude the force associated with the pressure gradient by establishing its balance with some volumetric force acting on the medium. At the same time, for example, in [27], [47], the magnitude of the dynamic pressure is already explicitly determined $p = \rho \text{div}\vec{u}$ through the magnitude of the
divergence of the velocity field of the compressible medium, taking into account the volumetric viscosity of this medium. Similar representations for pressure in the case of a medium far from equilibrium, in which the volume (or second) viscosity coefficient can be much higher than the coefficient of ordinary shear viscosity, are also given in [2], [34]. Moreover, in [27], [47] it is shown that the expression (79.1) in [34] for the rate of dissipation of the integral kinetic energy of the compressible medium is in contradiction with the equations of hydrodynamics and this is a direct consequence of the use in [34] for the pressure gradient of the representation following from the equilibrium thermodynamic relation, which includes pressure having a meaningful of elasticity [45]. Appendix B summarizes this proof obtained in [27], [47] and indicates the need for a more balanced use of the EOS of the medium in this connection.

**Summary**

An explicit complete analytical EOS for an arbitrary condensed media and EOS for water in the Mi-Gruneisen form are obtained. The last is presented as a dependence of pressure, the thermal part of the internal energy density, and the Gruneisen coefficient on water density and temperature. It is shown that a good correspondence between the obtained new analytical equation of state with observational data and the well-known tabular form of the EOS for water is achieved by taking into account the dependence of the effective exponent of the degree of potential of intermolecular interaction on the degree of compression. This allows one to use the ratio between pressure and internal energy to obtain an explicit form of the shock adiabatic. The latter is important for determining the explicit dependence of the Dyakov parameter, which is a key parameter, together with the Mach number when solving problems of shockwave stability [10]-[12]. It is shown that when using the isothermal EOS (30) to describe strong shock waves in water, it is necessary to consider the dependence of the exponent on the compression and
temperature [48], [49]. Indeed, the results presented in [48], [49] show the importance of this dependence for the interpretation of the non-monotonic dependence of the converging strong shockwave velocity versus the shock radius observed experimentally. The relation was also obtained between the exponent and the Gruneisen parameter. It was shown that this relation significantly depends on the type of intermolecular interaction potential, which in its turn varies according to the water compression. An accurate analytical solutions, obtained on the basis of first principles for the dependence of the degree of interaction potential on temperature and density, may also be useful in connection with the machine-learning interatomic potential models that allows for model materials and allows for calculation of forces and molecular dynamics simulations [50].

Acknowledgement

I wish to thank Yakov E. Krasik for drawing my attention to this problem, and for his support, fruitful discussions, and assistance in the manuscript editing. I also express my thanks to A. Virozub for providing simulation data. This research was supported by the Israeli Science Foundation Grant No. 492/18

Appendix A. Virial theorem generalization

1. Let us generalize the conclusion of the virial theorem proposed in [22] to the case of an arbitrary exponent \( \tilde{d} = \tilde{d}(r) \) of the power-law of potential energy of interaction between particles located at distances from each other \( r \):

\[
E_p \propto \frac{e^2}{r^{\tilde{d}}} 
\]  

(A1)
In (A1), as in [22], \( e \) is the charge of an electron, but unlike [22], where a Coulomb-type potential with a fixed value \( \tilde{d} = 1 \) is considered, here and further it will be assumed that the value \( \tilde{d} = \tilde{d}(r) \) can be a variable function, and not a constant value. At the same time, we will assume that the function tends to zero in the limit of small distances (which is similar to asymptotic freedom in elementary particle physics [24]), as well as in the limit of large distances:

\[
\tilde{d} \to 0, r \to 0 \quad \text{(A2)}
\]

\[
\tilde{d} \to 0, r \to \infty \quad \text{(A3)}
\]

We will use the equation of balance when the change of total energy is caused only by changes in energy at the boundaries of the system. In this case, the outer boundary of the system is determined by its volume, and the inner boundary corresponds in (A 1) to the limit \( r \to 0 \) taking into account the condition (A2).

For the first law of thermodynamics, we have a representation in the form of an energy balance equation in which the total energy of the system, represented as the sum of kinetic and potential energies \( E = E_K + E_p \):

\[
dE = TdS - pdV \quad \text{(A4)}
\]

Let us consider a similarity transformation in which all charges including the elementary charge \( e \) are changed by the factor \( \lambda_e = 1 + \varepsilon, \varepsilon << 1; e \to \lambda_e e \), all distances by the factor \( \lambda_r = 1 + \mu, \mu << 1; r \to \lambda_r r \) and all the energies by \( \lambda_\eta = 1 + \eta, \eta << 1; E \to \lambda_\eta E \) [22]. As in [22] the quantum of action \( h \) and the electron mass are assumed to be unchanged.
From the expression of the potential energy (A1) the following relation obtains:

$$\frac{e^2}{r^{\tilde{d}(r)}}(1 + \eta) = \frac{e^2(1 + \varepsilon)^2}{\exp[\tilde{d}(r)(1 + \mu)\ln(r(1 + \mu))] + O(\mu^2)} \approx \frac{e^2(1 + 2\varepsilon)}{1 + \mu[\tilde{d} + r \ln r \frac{d}{dr}(\tilde{d}(r)) + O(\mu^2)]}$$

or:

$$\eta = 2\varepsilon - \mu d - O(\mu^2),$$

$$d \equiv \left(\tilde{d} + \frac{d}{dz}\tilde{d}(z)\right); z \equiv \ln(\ln r) \quad (A5)$$

The relation (A 5) for the value $\tilde{d} = 1$ exactly coincides with the conclusion [22], and for the function $\tilde{d}(r)$ gives its generalization.

To obtain (A 5), it is taken into account that the potential energy (A 1) is considered outside the inner boundary at finite values $r$ when the function $\tilde{d}(r)$ is also finite. At the same time, (A 5) takes into account only the terms of the first order of smallness in terms of parameters $\varepsilon, \mu, \eta$ that determine the similarity transformation. Therefore, when converting to (A 5), only the first term of the specified Taylor series expansion $\tilde{d}(r(1 + \mu)) \approx \tilde{d}(r) + r\mu \partial \tilde{d}(r)/\partial r + (\mu^2)$ in degrees of $\mu$ for the function $\tilde{d}(r(1 + \mu))$ is taken into account.

The de Broglie wave-length, as all lengths, must change as $1 + \mu$ and thus momenta change as $(1 + \mu)^{-1}$ and kinetic energies as $E_K \rightarrow E_K(1 + \mu)^2 \approx E_K(1 - 2\mu + O(\mu^2))$[22]. However, these energies like all energies must change as $E_K \rightarrow E_K(1 + \eta)$, hence from this and from (A5):

$$\eta = -2\mu \quad (A6)$$

$$2\varepsilon = \mu(d - 2) \quad (A7)$$
In particular, for the value \( d_1 = d = 1 \) the ratio (A 7) coincides with the formula (31) of [22], and the ratio (A 6) coincides with the formula (30) of [22] for any values \( d \).

Let us treat, as in [22], the effect of the change of charges by a perturbation treatment when the energy change introduced by changing charge. In this case, the change in the total energy of the entire system \( \eta (E_K + E_\rho) \) should be equal to the sum of the changes caused by the change in charge at the inner boundary and outer boundaries. At the inner boundary, taking into account the condition (A2) in (A 5), only a change in charge leads to a change in potential energy, which as a result is equal to \( 2\varepsilon E_\rho \). In order to take into account the change in energy at the outer boundary of the system under consideration, which has an arbitrary finite volume, we use the consideration proposed in [22] in the form: “In order to arrive at the same configuration reached by similarity transformation, the volume must now be readjusted. This is done by a volume increase \( (1 + \mu)^3 \approx 1 + 3\mu \)”. Thus, energy of the system will decrease by amount equal \( 3\mu pV \), where \( p \) is the pressure on the external boundary of that volume and the energy balance equation is obtained in the form:

\[
\eta (E_K + E_\rho) = 2\varepsilon E_\rho - 3\mu pV
\]  

\( \text{(A8)} \)

After substituting in (A8) the equalities (A6), (A7) in the form \( \mu = 2\varepsilon l(d - 2); \eta = -4\varepsilon l(d - 2) \) and carrying out the corresponding simplifying transformations, we obtain a known form of representation of the virial theorem in the case when the potential energy of the interaction of particles is a homogeneous function of degree \( n = -d \) [1]:

\[
pV = \frac{2}{3} E_K + d \frac{E_\rho}{3}
\]  

\( \text{(A9)} \)
In contrast to the well-known conclusion of the virial theorem (A9) given in [1], in the representation obtained in (A9), the value \( d \) can already be an arbitrary function satisfying (A5) under the condition (A2). In the case when this value is \( d = 1 \) the ratio (A9) exactly coincides with the one derived in [22] (see (29) in [22]).

Thus, the ratio (A9) is obtained only on the basis of similarity transformations and the energy balance equation. At the same time, the assumptions about time averaging and about the uniformity of potential energy, which are common with the well-known derivation of the virial theorem [1], were not used.

From the comparison of the energy balance equation (A8) with the first law of thermodynamics (A4), it follows that the left part (A8) and the second term in its right part correspond exactly to the same terms of the equation (A4). This means that it is permissible to compare both the first terms in the right-hand sides of equations (A4) and (A8), and which follows the possibility of estimating the magnitude of the entropy perturbation caused by changes in the magnitude of charges during the similarity transformation. If in (A4), when describing the change in entropy in the form \( S \rightarrow \lambda S; \lambda = 1 + \delta, \delta \ll 1 \) use substitution \( dS \rightarrow \delta S \), then from the comparison with (A8) we get:

\[
\delta S = 2\varepsilon q_p;
\]

\[
q_p = \frac{E_p}{TS} \propto O(1)
\]

At the same time, depending on the sign of the magnitudes \( \varepsilon \) and \( E_p \), both an increase and a decrease in entropy is possible, due to the transformation of similarity associated with a change in charge. This does not contradict the law of increase, which is valid for closed systems, since
the estimate of the magnitude of the entropy change obtained in (A10) is associated precisely with its change at the inner boundary of the system under consideration.

Note also that, despite the exact coincidence of the first term in the right part (A8) with the similar term in the energy balance equation given in [22], there is a difference in the justification for the appearance of this term in this form. The qualitative explanation given in [22] proceeds from the idea that entropy remains unchanged during the considered similarity transformation.

On the contrary, the justification of the representation for the first term in the right-hand side (A8) in this paper is proved on the basis of a strict quantitative assessment, which is essentially based on the assumption (A2) about the nature of the asymptotic behavior of the interaction potential, which is analogous to the asymptotic freedom in the theory of elementary particles [24]. In the argumentation [22], it is not explicitly noted that the change in the total energy in the left side of the equation (A8) is due only to the presence of internal and external boundaries through which the energy flow is permissible. In this respect, it is the inner boundary, which has a zero measure of extent due to the point nature of the charge that can provide a change in entropy according to (A10). Thus, the decrease in entropy during the transformation of the similarity of the charge magnitude at the inner boundary can be interpreted as the dominance of the corresponding information factors compared in an analogy with the subject of the known studies [51]- [54].

2. Consider the case when the potential energy of interaction between the particles of the medium is a power function of distance, having the form:

\[ u_p(\vec{x})/u_o = (r/r_0)^\nu; r = |\vec{x}| \]  
(A11)
It is usually assumed that the value of the potential energy index \( n = \text{const} \) in (A 11) is constant when Euler's theorem on homogeneous functions \( \sum_{a=1}^{N} x_{a}^{n} \frac{\partial u_{p}}{\partial x_{a}} = n u_{p}(\bar{x}^{1}, \bar{x}^{2}, \ldots, \bar{x}^{N}) \) leads to a well-known representation of the virial theorem for a system of \( N \) interacting particles [1].

By definition, a function \( u_{p}(\bar{x}) \) is a homogeneous function of coordinates if the scale transformation of stretching or compression for all coordinates on which this function depends has the form

\[
\begin{align*}
    u_{p}(\lambda \bar{x}) &= \lambda^{n} u_{p}(\bar{x}); \\
    \bar{x} &= (x_{1}; x_{2}; \ldots; x_{N}) \quad (A 12)
\end{align*}
\]

At the same time, in (A 12) there can be any constant value \( \lambda \) of the scale conversion coefficient.

Consider the case when in the definition (A 12) the uniformity index \( n = n(\bar{x}) \) depends on the coordinates. We introduce the concept of locally homogeneous functions for which the relation (A 12) holds only for such magnitudes of the scale transformation coefficient that satisfy the additional condition \( \lambda = 1 \pm \varepsilon; \varepsilon \ll 1 \). To substantiate this statement, we use the well-known method of proving Euler's theorem on homogeneous functions. To do this, we differentiate the left and right sides of the relation (A 12) by the parameter \( \lambda \). This leads to equality:

\[
\sum_{a=1}^{N} \frac{\partial u_{p}(\lambda x_{1}; \ldots; \lambda x_{N})}{\partial (\lambda x_{a})} \frac{\partial (\lambda x_{a})}{\partial \lambda} = n \lambda^{n-1} u_{p}(\bar{x}) \quad (A 13)
\]
In the left part (A 13) we have \( \partial(\lambda x_a) / \partial \lambda = x_a; \partial u_p(\lambda x) / \partial(\lambda x_a) = \lambda^{-1} \partial u_p(\lambda x) / \partial x_a \). Therefore, from (A13) we get (since taking into account (A12) we have \( \partial u_p(\lambda x) / \partial x_a = \partial(\lambda^m u_p(\lambda)) / \partial x_a \)) in general when \( n = n(\bar{x}) \neq \text{const} \):

\[
\sum_{a=1}^{N} x_a \frac{\partial u_p(\bar{x})}{\partial x_a} + u_p(\bar{x}) x_a \frac{\partial n}{\partial x_a} \ln \lambda = n u_p(\bar{x}) \quad (A14)
\]

For any \( \lambda \) only in the case of a constant value \( n \) we obtain from (A14) the well-known statement of Euler’s theorem on homogeneous functions having a constant value of the degree of uniformity. In the case when this degree of uniformity \( n = n(\bar{x}) \) is no longer constant, we can consider a class of locally homogeneous functions for which only in the limit \( \lambda = 1 \pm \varepsilon_i; \varepsilon_i \to 0 \) of (A14) follows a modification of Euler’s theorem having the form:

\[
\sum_{a=1}^{N} x_a \frac{\partial u_p(\bar{x})}{\partial x_a} = n(\bar{x}) u_p(\bar{x}) \quad (A15)
\]

In particular, when equality \( n(\bar{x}) = -d(\bar{x}) \) is fulfilled, the exponent of local homogeneity is related to the exponent \( \tilde{d} \) of the potential of interaction of particles by the ratio (A5) or equation (1) of the main text.

**Appendix B The problem of closure and thermodynamic relations**

Let us consider the equations of hydrodynamics of a viscous compressible medium, which have the form:

\[
\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = -\frac{1}{\rho} \frac{\partial}{\partial x_i} \left( p - \left( \frac{\varepsilon + \eta}{3} \right) \text{div} \vec{u} \right) + \frac{\eta}{\rho} \Delta u_i \quad (B1)
\]
\[
\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0
\]  
(B2)

Based on the equations (B1) and (B2), an expression can be obtained for the time derivative of the integral kinetic energy of the flow of a viscous compressible medium. According to the definition, this energy has the form [34]:

\[
E_K = \frac{1}{2} \int d^3 x \rho \bar{u}^2
\]  
(B3)

Differentiating the energy value in (B3) by time, we obtain directly using (B1) and (B2) the following equation of the kinetic energy balance of the flow of a viscous compressible medium:

\[
\frac{dE_K}{dt} = -\eta \int d^3 x \left(\frac{\partial u_i}{\partial x_j}\right)^2 + \int d^3 x \rho \bar{u} \left(p - \left(\zeta + \frac{\eta}{3}\right)\text{div} \bar{u}\right)
\]  
(B4)

The balance equation (B4) in the limit of zero shear \(\eta\) and volumetric \(\zeta\) viscosities coincides with the one given in G. Lamb's book [55] for the case of compressible flows. It is equation (B4) that gives a generalization for the energy balance equation of the incompressible medium flow, given in [34] in the form of equation (16.3) when compressibility must be taken into account.

At the same time, in [34] it is stated that, taking into account the compressibility of the medium, the generalization of equation (16.3) is equation (79.1), which for the isothermal case has view:

\[
\frac{dE_K}{dt} = -\zeta \int d^3 x \text{div} \bar{u}^2 - \frac{\eta}{2} \int d^3 x \left\{\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \text{div} \bar{u}\right\}^2
\]  
(B5)

At the same time, the kinetic energy balance equation of the compressible medium given in [34] in the form of (B5), in contrast to (B4), no longer coincides with the balance equation given in G. Lamb's book in the zero viscosity limit. As a result, equation (B5) differs from the balance
equation (B4) obtained directly from the hydrodynamic equations (B1) and (B2). This means that equation (B5) contradicts equations (B1), (B2) and cannot be a generalization of the integral kinetic energy balance equation for the case of a compressible medium.

We show that the indicated contradiction of equation (B5) to the equations of the hydrodynamics of a compressible medium (B1), (B2) is the use of the thermodynamic relation (see below (B9)) for the pressure gradient used in the derivation (B5) based on the integral entropy balance equation. Indeed, to derive equation (B5) in [34], the integral entropy balance equation is used, which is obtained from the condition of conservation of the total integral energy, representing the sum of the integral kinetic and integral internal energy in the form:

$$E = E_k + E_i;$$
$$E_i = \int d^3x \rho \varepsilon_i$$  \hspace{1cm} (B6)

For this purpose, in [34], based on the equations of hydrodynamics of a compressible medium (B1) and (B2), the rate of change in time of the total energy density is obtained, which has the form:

$$\frac{\partial}{\partial t} \left( \frac{\rho u^2}{2} + \rho \varepsilon_i \right) = -\left( \frac{u^2}{2} + \frac{p}{\rho} + \varepsilon_i \right) \text{div}(\rho \mathbf{u}) - \rho (\mathbf{u} \cdot \nabla \mathbf{u}) \frac{u^2}{2} - \mathbf{u} \cdot \nabla p + \rho T \frac{\partial S}{\partial t} + u_i \frac{\partial \sigma_{ik}'}{\partial x_k} ;$$

$$\sigma_{ik}' = \eta \left( \frac{\partial u_k}{\partial x_i} + \frac{\partial u_i}{\partial x_k} - \frac{2}{3} \delta_{ik} \text{div} \mathbf{u} \right) + \varsigma \delta_{ik} \text{div} \mathbf{u}$$  \hspace{1cm} (B7)

For the derivation (In 7) in [34], an equation derived from the first law of thermodynamics \(d \varepsilon_i = T ds + p d\rho / \rho^2\) and the continuity equation (In 2) was used, which has the form:
\[
\frac{\partial \varepsilon_i}{\partial t} = T \frac{\partial s}{\partial t} - \frac{p}{\rho^2} \text{div}(\rho \ddot{u}) \quad (B8)
\]

In addition, and this is most significant in terms of understanding the difference between (B5) and (B4), in [34], a thermodynamic relation \( d(\varepsilon_i + \frac{p}{\rho}) = Ts + dp/\rho \), was used to transform into (B7) a term \( \ddot{u} \nabla p \), containing a pressure gradient, leading to a representation for the pressure gradient in the form:

\[
\ddot{u} \nabla p = \rho \ddot{u} (\varepsilon_i + \frac{p}{\rho}) - \rho T \ddot{u} s \quad (B9)
\]

After substituting (B9) into (B7) and from the condition of conservation of the total integral energy \( dE/dt = 0 \) in [34], the integral entropy \( S = \int d^3 x \rho s \) balance equation is obtained (see (49.6) in [34]), which in the isothermal case and for constant coefficients of shear and bulk (second) viscosity has the form:

\[
T \frac{dS}{dt} = \frac{\eta}{2} \int d^3 x \left( \frac{\partial u_k}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \text{div} \ddot{u} \right)^2 + \xi \int d^3 x \text{div} \ddot{u} \quad (B10)
\]

Further, in [34] from (B10), to obtain the kinetic energy balance equation in the form (B5), a well-known relation was used, performed for any mechanical system in the isothermal case \( T = T_0 = \text{const} \), which has the form:

\[
T_0 \frac{dS}{dt} = - \frac{dE_k}{dt} \quad (B11)
\]

Let us show that the relation (B11) can be fulfilled with the independent derivation of the balance equation (B4) for the integral kinetic energy and for the balance equation of the integral
entropy obtained as in [34] based on the condition of conservation of the integral total energy, but without using the thermodynamic relation (B9) for the pressure gradient. To do this, in addition, instead of (In 8) we will use the equation:

\[
\frac{\partial \rho \varepsilon}{\partial t} = T \frac{\partial (\rho s)}{\partial t} + \Phi \frac{\partial \rho}{\partial t}
\]  

(B12)

In this case, the Gibbs thermodynamic potential is used, which has the form:

\[
\Phi = \mu_i, N = \varepsilon_t + \frac{p}{\rho} - Ts;
\]

\[
d\varepsilon_t = Ts + \frac{p}{\rho^2} d\rho;
\]

\[
d\Phi = \frac{dp}{\rho} - sdT
\]  

(B13)

As a result, we obtain the integral entropy balance equation from the condition of conservation of the total integral energy [27], [47]:

\[
\frac{dE}{dt} = -\int \partial x \partial v \dot{J}_E + \frac{dS}{dt} - \dot{B} = 0; S = \int \partial x \partial s;  
\]

\[
\dot{J}_E = \dot{\bar{\varepsilon}} \left( \rho \left( \frac{\bar{u}_I^2}{2} + \phi + Ts \right) + p - \left( \frac{\zeta + \eta}{3} \right) \partial v \bar{u} \right) - \frac{\eta}{2} \nabla \bar{u} \nabla \bar{u}
\]

\[
\frac{dS}{dt} = \dot{B};
\]

\[
T_0 \dot{B} = \eta \int \partial x \left( \frac{\partial u_i}{\partial x_j} \right)^2 - \int \partial x \partial v \left( p - \left( \frac{\zeta + \eta}{3} \right) \partial v \bar{u} \right) - \int \partial x \Phi \partial v (\rho \bar{u})
\]  

(B15)

From the comparison (In 15) and (In 4) we obtain a generalization of the relation (In 11) in the form:
The representation (In 16) under the condition \( \Phi = \mu_{ch} N = \Phi_0 = const \) matches (B11). It generalizes it to the case of a variable number of particles \( N \) and a variable chemical potential \( \mu_{ch} \) when an additional condition in the form of is required to fulfill the relation (B11):

\[
\int d^3x \Phi \text{div} (\rho \ddot{u}) = 0 \tag{B17}
\]

Thus, the ratio (B11) is obtained based on the equations of hydrodynamics (B1), (B2) only when using the thermodynamic ratio (B12) without the need to apply the representation (B9) for the pressure gradient. Therefore, due to the direct contradiction of equation (B5) to the equations of hydrodynamics of a compressible medium (B1), (B2), which can be seen directly, it is possible to make a statement about a similar contradiction of the integral entropy balance equation (B10), if a fundamental relation (B11) is valid [34]. In turn, this necessarily leads to the conclusion that it is unacceptable to use the thermodynamic relation (B9) to describe the dynamic pressure gradient included in the hydrodynamic equations (B1) when deriving the integral entropy balance equation.

In this regard, it is necessary to revise the applicability of the representation for pressure following from the thermodynamic EOS in Eq. (B1) for the closure the hydrodynamics equations in all cases where this could be avoided, as in the above derivation of the integral entropy balance equation (B15). In contrast to Eq. (B10) (see also (49.6) in [34]), the EOS (B15) does not contradict the equations of hydrodynamics (B1), (B2) in their combination with the equation (B11), that is suggested to valid for any mechanical system [34].

**Appendix C. The Gruneisen parameter**
1. Using the definition of the Gruneisen parameter as

\[
\frac{1}{\rho} \left( \frac{\partial \rho}{\partial u} \right)_{\rho = \text{const}} = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \rho} \right)_{\rho = \text{const}} \left( \frac{\partial u}{\partial \rho} \right)_{\rho = \text{const}}^{-1} = \Gamma
\]

using (37) and (38), we obtain that on the Hugoniot shock adiabat this parameter reads

\[
\Gamma = \frac{2}{\delta - 1}, \quad |d| \neq 2
\]

\[
\Gamma = \frac{2}{3}, \quad |d| = 2. \quad (C1)
\]

The Gruneisen coefficient defined in (25) coincides with (C1) only when the condition imposed on the compression in the form \(\delta = \delta_d \equiv 1 + 6/|d|\) is fulfilled. The dependence of the Gruneisen parameter on compression in (C1) qualitatively coincides with the estimate of this parameter presented in [31], which monotonically decreases with increasing compression at sufficiently large compressions (see Fig. 12(b) in [31]).

To obtain representation (31) for the Gruneisen parameter in the form \(\Gamma = c_f^2 \beta / c_V\), we use the following form of the specific heat capacity \(c_V\), which was obtained from the virial theorem in the form (14), and the relation \(\alpha \frac{p}{\rho} = \beta c_f^2\) [see (C8) below]:

\[
c_V = \left( \frac{\partial u}{\partial T} \right)_{\rho = \text{const}} = \beta \rho \left( 1 + \frac{3}{|d|} \right) + 3 \frac{k}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{|d|} \right); \quad \alpha = \frac{1}{\rho} \left( \frac{\partial p}{\partial T} \right)_{\rho = \text{const}} \quad (C2)
\]

\[
c_p = \left( \frac{\partial (u+p/\rho)}{\partial T} \right)_{p = \text{const}} = \beta \rho \left( 1 + \frac{3}{|d|} \right) + 3 \frac{k}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{|d|} \right); \quad \beta = \frac{1}{\rho} \left( \frac{\partial p}{\partial T} \right)_{p = \text{const}} \quad (C3)
\]

Now, the adiabatic exponent reads

\[
\gamma = \frac{c_p}{c_V} = \frac{a_1 + g}{b_1 + g}, \quad a_1 = \beta \rho \left( 1 + \frac{3}{|d|} \right), \quad b_1 = \alpha \frac{3p}{|d| \rho}; \quad g = \frac{3k}{m_{H_2O}} \left( \frac{1}{2} - \frac{1}{|d|} \right). \quad (C4)
\]
Using (C4) and the condition on the adiabatic index $\gamma > 1$, we obtain the following limitation on parameter $d$:

$$|d| > 3 \left( \frac{\alpha}{\beta} - 1 \right) = 3 \left( \frac{\rho c_T^2}{p} - 1 \right).$$  \hspace{1cm} (C5)

The relation $\frac{p}{\rho} = \beta c_T^2$ is obtained by considering the known relations [19] (see Formulas (16.9) and (16.10) on page 74 in [19]):

$$c_p - c_V = -T \left( \frac{\partial V}{\partial T} \right)_{p=\text{const}}^2 \left( \frac{\partial V}{\partial p} \right)_{T=\text{const}}$$  \hspace{1cm} (C6)

$$c_p - c_V = -T \left( \frac{\partial p}{\partial T} \right)_{V=\text{const}}^2 \left( \frac{\partial p}{\partial V} \right)_{T=\text{const}}.$$  \hspace{1cm} (C7)

After equating the right hand sides of (C6) and (C7),

$$\frac{p^2 a^2}{\rho^2 B^2} = \left( \frac{\partial p}{\partial \rho} \right)^2_{T=\text{const}} = c_T^4$$  \hspace{1cm} (C8)

From (C8), we obtain the relation $\frac{p}{\rho} = \beta c_T^2$. Relation (C8) includes the value of the isothermal velocity of sound $c_T$ [27]. This value for the isothermal EOS of water (29) has the form

$$c_T^2 = c_{0T}^2 \delta^{n-1}.$$  \hspace{1cm} (C9)

As a result, using (C9) and considering (C4), we obtain for $\gamma = \frac{c_p}{c_V} > 1$

$$|d| > 3 \left( \frac{\rho_0 c_0^2 \delta^n}{p} - 1 \right).$$  \hspace{1cm} (C10)

In the case where the pressure in (C10) satisfies the isothermal EOS (29), from (C10) and (29) in the limit $\delta^n \gg 1 ; p \gg p_0$, the relation $p \approx \rho_0 c_0^2 \delta^n / n$ becomes valid and the condition (C10) is reduced to the form
\[ n < 1 + \frac{|d|}{3}; o r |d| > 3(n - 1) . \]  \hspace{1cm} (C11)

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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