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THERMODYNAMIC EQUATION OF STATE USED TO DESCRIBE THE BEHAVIOR OF A POROUS MIXTURE UNDER HIGH PRESSURES AND TEMPERATURES

R. K. Bel'kheeva

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Equations of state of condensed species and air filling the pore space and an equation of state of the mixture are presented in a unified manner (in the form of the Mie–Grüneisen equation). Applicability of such an equation of state for air in the range of high pressures and temperatures is validated by comparisons of shock adiabats calculated with the use of this equation and available data in the literature. The thus-derived equation of state of a thermodynamically equilibrium mixture, which takes into account the characteristics of the species and their mass concentrations, offers a fairly accurate description of the behavior of a porous medium.

Key words: *equation of state, porous mixture, shock adiabat.*

Introduction. The description of various mixtures by methods of mechanics of continuous media involves the notion of interacting and interpenetrating continua. In this theory, each continuum is a phase or a species of the mixture and fills the entire volume. Reduced density (mass of the species in a unit volume of the medium), velocity, and other parameters are determined for each continuum. The mixture as a whole is characterized by density and mean-mass velocity.

In the general case, the system of equations of motion of the mixture consisting of m species includes m equations of conservation of mass, m equations of conservation of momentum, and m equations of conservation of energy; the system is closed by m equations of state relating thermodynamic parameters of each material and by equations that describe the conditions of the joint motion and deformation of the phases.

In the case of propagation of strong shock waves initiating phase transitions in solids, it is usually assumed that the properties of solids are close to the properties of fluids; therefore, the condition of identical pressures of the phases is commonly used as a condition of joint motion. Several methods were proposed in [1] to describe the relation between the pressure of the mixture and the pressures of the species. The area of applicability of these equations was found to be determined by the magnitude of porosity of the material examined. It was demonstrated that the best approximation for a porous substance in the range of high pressures and temperatures is the widely used condition of identical pressures of the phases.

If the mixture is thermodynamically equilibrium, its motion can be described as the motion of one continuum with a special equation of state, which takes into account the properties of the species of the mixture and their concentrations. As a result, the number of equations is substantially reduced.

The method considered in [2–5] and other papers implies that the equations of state of the species are similar to the equations for these substances in the free state. Lyakhov [2] derived such an equation for a three-species mixture with a barotropic equation of state for the species. Dunin and Surkov [3] found a dependence of the mean pressure of the solid phase on porosity and pressure inside pores under static loading of a solid porous mixture. Nigmatulin [4] derived an equation of state of an equilibrium mixture of a calorically perfect gas and an incompressible solid. An equation of state of a mixture of two condensed species in the form of the Mie–Grüneisen equation was proposed in [5]. It is the latter model that is developed in the present paper.

Novosibirsk State University, Novosibirsk 630090; rumia@post.nsu.ru. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 48, No. 5, pp. 53–60, September–October, 2007. Original article submitted December 29, 2005; revision submitted November 8, 2006.

Equations of State Used. It is assumed that there exists a shock adiabat of an equilibrium porous mixture of m species, each of them being described by an equation of state in the Mie–Grüneisen form. The system is considered to be in equilibrium if the following conditions are satisfied: $P_i = P$, $T_i = T$, and $u_i = u$, where P_i, T_i, and u_i are the pressure, temperature, and mass velocity of the ith species; P, T, and u are the pressure, temperature, and mass velocity of the mixture.

The pressure of a solid in the region of explosive loads is normally presented as a sum of two terms:

$$P = P_{\text{el}} + P_{\text{th}}$$

(P_{el} is the elastic pressure, $P_{\text{th}} = \gamma\rho E_{\text{th}}$ is the thermal pressure, γ is the Grüneisen coefficient, ρ is the density of the substance, and E_{th} is the thermal energy). The internal energy is also presented as a sum of two terms:

$$E = E_{\text{el}} + E_{\text{th}}.$$

Here E_{el} is the elastic energy of compression

$$E_{\text{el}} = \int\limits_{\rho_0}^{\rho} \frac{P_{\text{el}}}{\rho^2}\, d\rho,$$

ρ_0 is the density at the initial time, $E_{\text{th}} = cT$ is the thermal component of the internal energy, and c is the specific heat.

Equation of State in the Mie–Grüneisen Form for Air. To reach a unified description of the porous mixture and all its species, the equation of state of air inside the pores is also presented in the form of the Mie–Grüneisen equation. The elastic part of pressure is written in the Tate form as

$$P_{\text{a,el}} = A_a[(\rho_a/\rho_{\text{a},0})^{n_a} - 1].$$

Here ρ_a and $\rho_{a,0}$ are the density and initial density of air, $A_a = c_{s,0}^2\rho_{\text{a},0}/n_a$ and n_a are constants of the equation, and $c_{s,0}$ is the velocity of sound under standard conditions; the subscript a refers to air.

Two series of computations were performed to justify the applicability of this equation:

1. $A_a = \text{const}$ and $c_a = \text{const}$;
2. $A_a = \text{const}$ and $c_a = c_a(T(P))$.

In case 2, the specific heat of air c_a in the range of pressures and temperatures inherent in shock waves was obtained as follows. The shock adiabats for air are presented in a tabular form in [6]. The specific heats of air for pressures and temperatures indicated in [6] were chosen from tables presented in [7]. The dependence of c_a on temperature in the shock wave is approximated by the function

$$c_a(T(P)) = a_0 + b_0(T - 300)^2 + c_0(T - 300)^3 \tag{1}$$

and is plotted in Fig. 1. Here $a_0 = 0.7176$ kJ/(kg·K), $b_0 = 8 \cdot 10^{-8}$ kJ/(kg·K), and $c_0 = 3.8 \cdot 10^{-12}$ kJ/(kg·K). With varied γ_a and n_a, it was found by a numerical (iterative) method that the best agreement between the shock adiabats and the data of [6] is reached with the Grüneisen coefficient for air $\gamma_a = 0.16$ and compressibility factor $n_a = 2.2$. It should be noted that γ in a similar equation of state of detonation products of condensed explosives [6] varies from 1/5 to 1/3 at low densities (ideal gas) and from 0.7 to 1.0 if the density of detonation products is $\rho > 2$ g/cm^3.

Figure 2 shows the shock adiabats for air (in the coordinates mass velocity–shock-wave velocity, mass velocity–pressure, and density–pressure) calculated by the equation of state proposed here, and also the data of [6]. The best agreement (as compared with the data of [6]) can be reached if the factor n_a with increasing pressure is varied from 2.0 to 3.1 (points in Fig. 2).

Figure 2 also shows the shock adiabat for air calculated by the equation of state for an ideal gas $P = \gamma\rho c(T - T_0)$ ($\gamma = 1.4$).

A comparison of the shock adiabats for air calculated by the proposed equation of state and the data of [6] allows us to conclude that the equation of state in the Mie–Grüneisen form is applicable for air.

Equation of State of the Porous Substance. The values of the parameters listed in Table 1 were used to obtain equations of state for porous copper, porous graphite, and a porous mixture of graphite and copper. The shock adiabats for solids calculated with the use of these parameters are in good agreement with the shock adiabats obtained in [8–11].

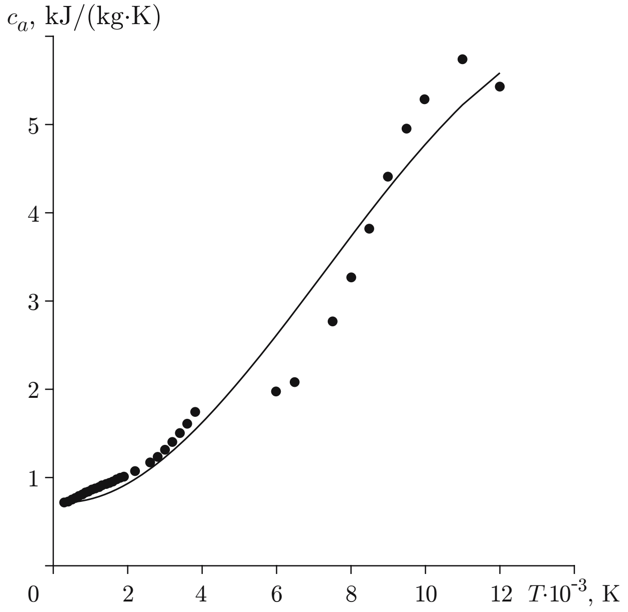

Fig. 1. Specific heat of air versus temperature in the shock wave: the points refer to the data of [7] and curve refers to the computation by Eq. (1).

The equations of state of the species are normalized in a manner that ensures zero values of the pressures and energies of the phases under standard conditions ($P = 0.1$ MPa and $T = 300$ K):

$$P = A_i[(\rho_{ii}/\rho_{ii,0})^{n_i} - 1] + \gamma_i\rho_{ii}c_i(T - 300), \qquad E = E_{\text{el},i} + c_i(T - 300).$$

Here A_i and n_i are compressibility constants, ρ_{ii} and $\rho_{ii,0}$ are the true density and the initial true density, c_i is the specific heat, and γ_i is the Grüneisen coefficient of the ith species. With such normalization and for a quiescent state of the medium ahead of the front of the normal shock wave, the Hugoniot equations for an equilibrium mixture have the form

$$\rho_0 D = \rho(D - u), \qquad P = \rho_0 D u, \qquad E = (P/2)(1/\rho_0 - 1/\rho), \tag{2}$$

where ρ, ρ_0, u, P, and E are the density, initial density, mass velocity, pressure, and energy of the medium behind the shock-wave front; D is the velocity of the shock-wave front. Supplementing system (2) with two equations of state of the medium

$$P = P(\rho, T), \qquad E = E(\rho, T), \tag{3}$$

we obtain a system of five equations for six unknowns. Setting the value of velocity of the medium behind the shock-wave front, system (2), (3) provides the values of all parameters.

The density of the m-species mixture is calculated by the formula $1/\rho = \sum\limits_{i=1}^{m} x_i/\rho_{ii}$, and the heat capacity is described by the formula $c = \sum\limits_{i=1}^{m} x_i c_i$, where x_i are the mass concentrations of the species. For the mixture considered, we used $\gamma = \sum\limits_{i=1}^{m} x_i\gamma_i$ and $n = \sum\limits_{i=1}^{m} x_i n_i$.

The equations of state (3) have the form

$$P = P_{\text{el}} + \gamma\rho E_{\text{th}}, \qquad E = E_{\text{el}} + E_{\text{th}}, \tag{4}$$

where

$$P_{\text{el}} = A\Big[\Big(\frac{\rho}{\rho_0}\Big)^n - 1\Big], \qquad E_{\text{th}} = c(T - 300), \qquad E_{\text{el}} = \int\limits_{\rho_0}^{\rho} \frac{P_{\text{el}}}{\rho^2}\,d\rho.$$

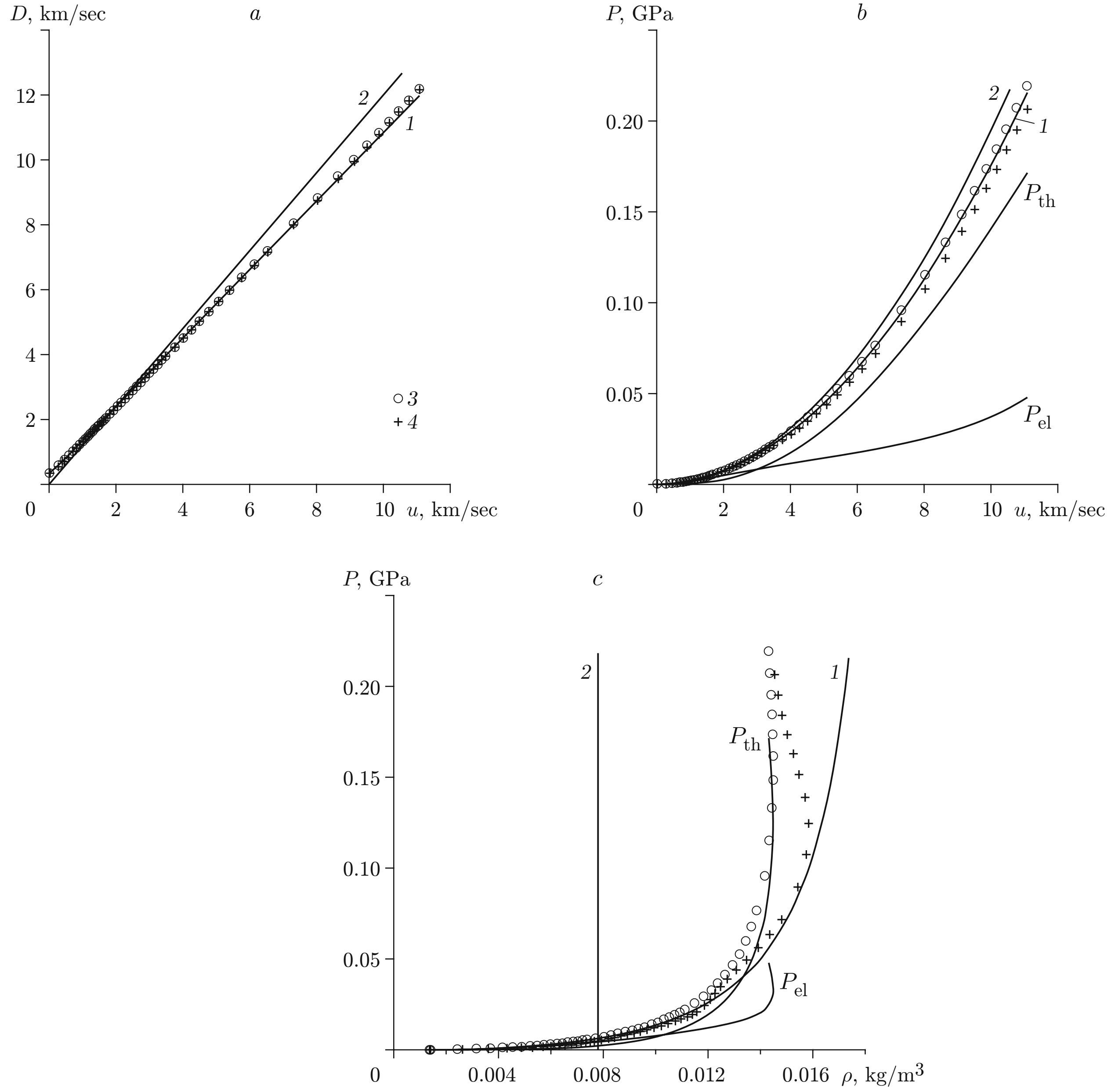

Fig. 2. Shock adiabat of air in the coordinates mass velocity–shock-wave velocity (a), mass velocity–pressure (b), and density–pressure (c): curves 1 and 2 refer to $n_a = 2.2$ and ideal gas, respectively; points 3 refer to $n_a = 2.0$–3.1 and points 4 refer to the data of [6].

TABLE 1

Parameters of Equations of State for Air, Copper, and Graphite.

Substance	$\rho_{ii,0}$, kg/m^3	A_i, Pa	n_i	c_i, kJ/(kg · K)	γ_i
Air	1.3	$0.695 \cdot 10^{-3}$	2.2	0.718	0.16
Copper	$8.93 \cdot 10^3$	$347.5 \cdot 10^8$	4.0	0.382	2.00
Graphite	$2.26 \cdot 10^3$	$120.0 \cdot 10^8$	4.0	0.680	2.00

TABLE 2

Porosity and Mass Concentration of Air in Porous Copper

$\varkappa$	x_a
0.885	0.00001898
0.819	0.00003229
0.708	0.00006025
0.643	0.00008111
0.505	0.00014319

TABLE 3

Porosity and Mass Concentration of Air in Porous Graphite

$\varkappa$	x_a
0.98	0.00001094
0.82	0.00012890
0.78	0.00016100

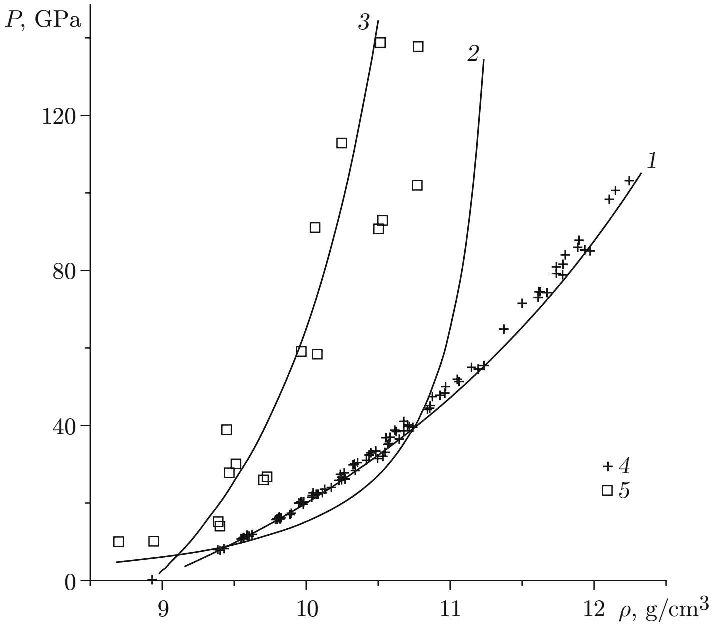

Fig. 3. Shock adiabats for solid (1 and 4) and porous ($\varkappa = 0.643$) (2, 3, and 5) copper: curves 2 and 3 refer to the calculations by the equation of state for a two-species mixture and by the equation of state for copper loaded from the initial porous state, respectively; points 4 and 5 refer to the data of [8].

The constants A and the initial density ρ_0 in the equation of state of the mixture are determined in the form

$$\frac{1}{A} = \sum_i \frac{x_i}{A_i}, \qquad \frac{1}{\rho_0} = \sum_i \frac{x_i}{\rho_{ii,0}}. \tag{5}$$

Here summation is performed over all species. Several methods were proposed in [5] to express A via the constants A_i and the mass concentrations of the species. Dependences (5) were found to offer a highly accurate description of the behavior of the mixture of condensed species under shock-wave loading in the range of low pressures, and the expressions for the same constants have the form

$$\frac{1}{A} = \sum_{i_c} \frac{x_i}{A_i}, \qquad \frac{1}{\rho_0} = \sum_{i_c} \frac{x_i}{\rho_{ii,0}} \tag{5$'$}$$

(summation is performed only over condensed species) in the range of high pressures.

First we studied the effect of porosity on the equation of state of the porous substance. For this purpose, a numerical (iterative) method was applied to the equations of state (4), (5) and (4), (5′) to calculate the shock adiabats for copper and graphite with different values of porosity (the porosity $\varkappa$ is understood as the ratio of the initial density of the mixture to the density of a monolith of the same composition), and a comparison with the data of [8–11] was performed. The compositions of the examined mixtures are given in Tables 2 and 3.

Figure 3 shows a shock adiabat of porous copper ($\varkappa = 0.643$) in the coordinates density–pressure. The shock adiabat calculated by Eqs. (4) and (5) (curve 2) is in good agreement with the data of [8] in the range of

TABLE 4

Characteristics of a Porous Mixture of Graphite and Copper

$\varkappa$	x_a	m_a	$x_{\rm gr}$	$x_{\rm Cu}$
1.0	0	0	0.20	0.8
1.0	0	0	0.40	0.6
1.0	0	0	0.60	0.4
1.0	0	0	0.80	0.2
0.8	0.000079	0.121	0.40	0.6
0.8	0.000058	0.092	0.20	0.8
0.8	0.000045	0.073	0.08	0.92
0.7	0.000099	0.147	0.20	0.8
0.7	0.000077	0.118	0.08	0.92

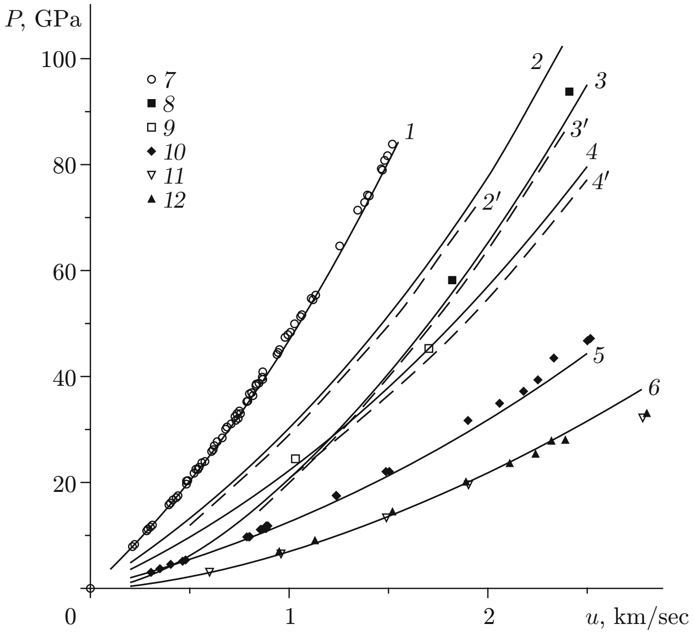

Fig. 4. Shock adiabats of the mixture: solid copper (1 and 7); solid mixture of graphite (20%) and copper (2 and 2′); porous mixture of graphite (8%) and copper ($\varkappa = 0.8$) (3, 3′, 8, and 9); solid mixture of graphite (40%) and copper (4 and 4′); solid graphite (5 and 10); porous graphite ($\varkappa = 0.8$) (6, 11, and 12); curves 1–6 refer to the data calculated in the present work and curves 2′–4′ refer to the data calculated in [12]; points 7 refer to the data of [8]; points 8 and 9 refer to the experimental data of [12] (without and with diamond observed in the tests, respectively); points 10, 11, and 12 refer to the data of [9], [10], and [11], respectively.

low pressures, and the shock adiabat calculated by Eqs. (4) and (5′) (curve 3) provides good agreement in the range of high pressures. An analysis of calculation results allows the following conclusions to be drawn: in the case of shock-wave loading of a porous substance, there exist nonequilibrium areas corresponding to the states of the substance before the beginning of pore filling (curve 2 in the range of low pressures); these areas are described by the equations of state of the mixture (4) and (5). Then, the overcompressed solid substance enters the pores, and the "final" adiabat is described by the equation of state of the solid loaded from the initial porous state.

Equation of State of a Porous Mixture of Two Condensed Species. The effect of porosity on the equation of state of a porous mixture of two condensed species (copper and graphite) was examined. As in the case described above, Eqs. (4) and (5′) were applied to calculate the shock adiabats of the mixtures with different concentrations of copper, graphite, and air, and the results were compared with the calculations of [12]. The compositions of the mixtures used are given in Table 4 (m_a is the volume concentration of air; $x_{\rm gr}$ and $x_{\rm Cu}$ are the mass concentrations of graphite and copper, respectively).

A comparison of all calculated shock adiabats with the data of [8–12] (Fig. 4 shows only some calculated results) allows us to conclude that the proposed equation of state in the form (4), (5′) is applicable for the description of porous mixtures. Thus, by an example of an equilibrium three-species mixture, it is demonstrated that the motion of such a mixture can be described by a system of equations of a single-phase continuous medium with a certain complex equation of state determined by the properties of the species and their concentrations.

Conclusions. The study performed allows the following conclusions to be drawn.

In the case of strong shock waves, the equation of state in the Mie–Grüneisen form can be used for air.

If the motion of the species relative to each other is ignored, a porous mixture of several condensed substances in thermodynamic equilibrium can be described as a single-phase continuous medium with the equation of state in the Mie–Grüneisen form with parameters expressed in terms of the corresponding parameters of the species.

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