EFFECTIVE THERMODYNAMIC FUNCTIONS OF A GAS WITH SOLID PARTICLES

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Using the relaxation formalism of nonequilibrium thermodynamics, a dynamic equation of state and hyperbolic thermal-conductivity equation are derived for a gas with solid particles.

Let a gas contain solid particles having a temperature ξ. The change of this temperature may be described by the phenomenological equation

$$\frac{d\xi}{dt} = LA. \tag{1}$$

We note that in the general case ξ may play the role of some internal relaxation parameter (reaction coordinate, rotational or vibrational temperature of gas molecule, order parameter, etc.) [1-3]. In this sense, the problem under consideration is more general and is not limited solely to the description of thermal relaxation in a dispersed system.

If the system undergoes change, then for a pair of conjugate thermodynamic parameters x and y one can write the equation of the process $y = y(x, \xi)$. For $\xi = 0$ this equation describes a sequence of equilibrium states (quasistatic process). In the approximation linear in δx and $\delta \xi$, for y and A we may write

$$\delta y = \left(\frac{\partial y}{\partial x}\right)_\xi \delta x + \left(\frac{\partial y}{\partial \xi}\right)_x \delta \xi, \tag{2}$$

$$A = \left(\frac{\partial A}{\partial x}\right)_\xi \delta x + \left(\frac{\partial A}{\partial \xi}\right)_x \delta \xi. \tag{3}$$

Here the partial derivatives refer to equilibrium states in which $A = 0$. Introducing the time-differentiation operator $D = d/dt$ and considering Eq. (3), we rewrite Eq. (1) in the form

$$(1 + \tau_x D)\,\delta\xi = L\tau_x \left(\frac{\partial A}{\partial x}\right)_\xi \delta x, \tag{4}$$

where $\tau_x = [L(\partial A/\partial\xi)_x]^{-1}$ is the particle thermal-relaxation time. Using the Jacobian, we write

$$\left(\frac{\partial A}{\partial T}\right)_\xi = \frac{\partial(A, \xi)}{\partial(A, x)} \cdot \frac{\partial(A, x)}{\partial(x, \xi)} = -\left(\frac{\partial\xi}{\partial x}\right)_A \left(\frac{\partial A}{\partial\xi}\right)_x, \tag{5}$$

$$\left(\frac{\partial y}{\partial x}\right)_A - \left(\frac{\partial y}{\partial x}\right)_\xi = \frac{\partial(y, A)}{\partial(x, \xi)} \cdot \frac{\partial(x, \xi)}{\partial(x, A)} - \left(\frac{\partial y}{\partial x}\right)_\xi = \left(\frac{\partial y}{\partial\xi}\right)_x \cdot \left(\frac{\partial\xi}{\partial x}\right)_A. \tag{6}$$

Substituting $(\partial\xi/\partial y)_A$ from Eq. (6) into Eq. (5), and substituting the expression thus obtained for $(\partial A/\partial\xi)_x$ into Eq. (4), we eliminate $\delta\xi$ from Eq. (2), writing the effective thermodynamic derivative $\delta y/\delta x$ in operator form:

$$\left(\frac{\partial y}{\partial x}\right) = \left(\frac{\partial y}{\partial x}\right)_\xi + \frac{\left(\frac{\partial y}{\partial x}\right)_A - \left(\frac{\partial y}{\partial x}\right)_\xi}{1 + \tau_x D}. \tag{7}$$

For a monochromatic sound wave the eigenvalue of the operator D is equal to $i\omega$ and Eq. (7) gives the results of [3].

We now use Eq. (7) to calculate the effective adiabatic index $\hat{k}$ of the mixture of gas and solid particles. In this case, $y = p$, $x = V$, and the partial derivatives are defined from the equation of an adiabatic process $pV^k = $ const:

Instantaneous compression — $(\partial p/\partial V)_\xi = -(p/V)k_\infty$ (pure gas);

Equilibrium compression — $(\partial p/\partial V)_A = -(p/V)k_0$ (equilibrium mixture);

Nonequilibrium compression — $(\partial p/\partial V)_{ad} = -(p/V)\hat{k}$.

It follows from Eq. (7) that

$$\hat{k} = k_\infty + \frac{k_0 - k_\infty}{1 + \tau_V D} . \tag{8}$$

We use operator equation (8) to establish the relationship between pressure and volume for nonequilibrium compression of the mixture of gas with solid particles. Considering that $p = p[V(t)]$, we write

$$\hat{k} = k_\infty + \frac{k_0 - k_\infty}{1 + \tau_V D} = -\frac{V}{p} \cdot \frac{dp}{dV} = -\frac{V}{p} \cdot \frac{\dot{p}}{\dot{V}} . \tag{9}$$

Performing formal algebraic transformations and differentiating with respect to time, we obtain the dynamic equation of adiabatic states of the system:

$$\ddot{p}V + \dot{p}\left[(k_\infty + 1)\dot{V} + \frac{V}{\tau_V}\right] + k_\infty p \left[\ddot{V} + \frac{V}{\tau_p}\right] = 0. \tag{10}$$

In Eq. (10) it is considered that $k_\infty k_0^{-1} = \tau_V \tau_p^{-1}$. Now, with the aid of Eqs. (3) and (5), Eq. (4) can be reduced to the integral equation

$$\delta\xi = \frac{1}{\tau_x} \left(\frac{\partial\xi}{\partial x}\right)_A \int_0^{\tau_0} \delta x(t)\,dt - \frac{1}{\tau_x} \int_0^{\tau_0} \delta\xi(t)\,dt.$$

Using the method of averaging functional corrections in the first approximation, we obtain [4]

$$\delta\xi = \frac{\dfrac{\tau_0}{\tau_x}}{1 + \dfrac{\tau_0}{\tau_x}} \, \delta x.$$

Now using this relationship to eliminate $\delta\xi$ from Eq. (2) and considering Eq. (6), we have

$$\frac{\partial y}{\partial x} = \left(\frac{\partial y}{\partial x}\right)_\xi + \left[\left(\frac{\partial y}{\partial x}\right)_A - \left(\frac{\partial y}{\partial x}\right)_\xi\right]\left(1 + \frac{\tau_x}{\tau_0}\right)^{-1},$$

whence it is evident that the eigenvalue of the operator D is equal to τ_0^{-1}. Comparison of calculations with this approximation and calculations with exact solutions of Eq. (10) shows good agreement.

We note that Eq. (10) may be obtained from the equations of the first law of thermodynamics, convective Newtonian heat transfer, and state. Thus, expansion (3) is fulfilled in that region where Newton's law $q = \alpha(T_\infty - T_s)$ is valid.

We will now calculate the heat capacity of the nonequilibrium mixture of gas and solid particles. Expressing the heat capacity in terms of the entropy, on the basis of Eq. (7) we write

$$\hat{C}_z = T\left(\frac{\partial\hat{S}}{\partial T}\right)_z = T\left(\frac{\partial S}{\partial T}\right)_{\xi z} + \frac{T\left(\dfrac{\partial S}{\partial T}\right)_{Az} - T\left(\dfrac{\partial S}{\partial T}\right)_{\xi z}}{1 + \tau_\tau D} . \tag{11}$$

Here z characterizes a thermodynamic process. Considering in Eq. (11) that $S = S_\infty + S_0$,

$$T\left(\frac{\partial S}{\partial T}\right)_{\xi z} = \left(\frac{\partial S_\infty}{\partial T}\right)_z T = C_{z\infty}, \quad T\left(\frac{\partial S}{\partial T}\right)_{Az} = T\left(\frac{\partial S_0}{\partial T}\right)_z = C_{z0},$$

we finally obtain

$$\hat{C}_z = C_{z\infty} + \frac{C_{z0} - C_{z\infty}}{1 + \tau_\tau D} . \tag{12}$$

In this approximation τ_T is the isothermal particle relaxation time (particle relaxation temperature at constant gas temperature). If we limit ourselves to small Peclet numbers, where convective heat transfer connected with the mean motion of the medium is significant [5], on the basis of Newton's law we may take $\tau_T = C_s(\alpha f^{(s)})^{-1}$.

We will consider the heat transfer of some volume V of the mixture, limited by a closed surface f, with the surrounding medium. Taking z = p = const in Eq. (12), we write the thermal balance of the volume of mixture in question:

$$\int_V \hat{c}'_p \dot{T}\, dV = \oint_f \mathbf{q} \cdot d\mathbf{f}. \tag{13}$$

Applying the Gauss–Ostrogradskii theorem to Eq. (13) and expanding the action of the operator $\hat{c}_p$ from Eq. (12),

$$\hat{c}'_p = \rho \hat{c}'_p = \varepsilon c'_{p\infty} + \rho_V c'_s \frac{1}{1 + \tau_\tau D} , \tag{14}$$

we obtain the local equation of thermal balance:

$$\varepsilon c'_{p\infty} \tau_\tau \frac{\partial^2 T}{\partial t^2} + (\varepsilon c'_{p\infty} + \rho_V c'_s) \frac{\partial T}{\partial t} = -\operatorname{div}(\mathbf{q} + \tau_\tau \dot{\mathbf{q}}). \tag{15}$$

If we assume that for the dispersed medium Fourier's law

$$\mathbf{q} = -\lambda \nabla T \tag{16}$$

is valid, where λ is the thermal conductivity of the dispersed system, then from Eq. (15) there follows the hyperbolic thermal-conductivity equation

$$\varepsilon c'_{p\infty} \tau_\tau \frac{\partial^2 T}{\partial t^2} + (\varepsilon c'_{p\infty} + \rho_V c'_s) \frac{\partial T}{\partial t} = \lambda \left(1 + \tau_\tau \frac{\partial}{\partial t} \right) \nabla^2 T. \tag{17}$$

In Eq. (16), λ is a phenomenological coefficient and naturally cannot be calculated by thermodynamic methods. Statistical methods are required to solve the problem. Such an approach was developed in the works of Buevich, in particular, [6, 7]. In [5], which is a continuation of those studies, the spectral concepts of temperature fields in the medium and particles are analyzed in detail. It is shown that to an accuracy of terms of the order of the frequency squared, the temperature distribution in the medium is described by a hyperbolic equation:

$$\rho_V c'_s \sigma^{(1)} \frac{\partial^2 T}{\partial t^2} + (\varepsilon c'_{p\infty} + \rho_V c'_s) \frac{\partial T}{\partial t} = \lambda_\infty \beta_0 \left(1 + \frac{\beta^{(1)}}{\beta^{(0)}} \cdot \frac{\partial}{\partial t} \right) \nabla^2 T. \tag{18}$$

If we consider that τ_T is related to τ_p by the formula $\tau_T = \tau_p[(\varepsilon c'_{p\infty} + \rho_V c'_s)/\varepsilon c'_{p\infty}]$, then Eq. (17) takes the form

$$(\rho_V c'_s + c'_{p\infty}\varepsilon) \tau_P \frac{\partial^2 T}{\partial t^2} + (\varepsilon c'_{p\infty} + \rho_V c'_s) \frac{\partial T}{\partial t} = \lambda \left(1 + \tau_\tau \frac{\partial}{\partial t} \right) \nabla^2 T. \tag{19}$$

From Eq. (18) and (19) it is evident that $\lambda = \lambda_\infty \beta^{(0)}$, $\beta^{(1)}/\beta^{(0)} = \tau_T$, and $\sigma^{(1)} = [1 + (c'_{p\infty}\varepsilon/\rho_V c'_s)]\tau_p$, while for $c'_{p\infty}\varepsilon \ll \rho_V c'_s$, $\sigma^{(1)} = \tau_p$. The isobaric relaxation time can be calculated for

$$\tau_p = \tau_T \frac{c_{p\infty} \rho_\infty \varepsilon}{c_{p\infty}\rho_\infty\varepsilon + c_s\rho_s(1-\varepsilon)} = \frac{c_s\rho_s d}{6\alpha} \cdot \frac{c_{p\infty}\rho_\infty\varepsilon}{c_{p\infty}\rho_\infty\varepsilon + c_s\rho_s(1-\varepsilon)} . \tag{20}$$

In [8] the thermal conductivity in a boiling layer was described by a hyperbolic thermal-conductivity equation of the form

$$\tau_\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \frac{\lambda}{(\rho c)_{hc}} \nabla^2 T. \tag{21}$$

However, as is evident from Eqs. (18) and (19), the transformation to Eq. (21) is not always justifiable.

Finally, we note that the normal thermodynamic relationships exist between the operator functions. Thus, the specific heat capacity ratios $\hat{c}_p = c_{p\infty} + (c_{p0} - c_{p\infty})(1 + \tau_T D)^{-1}$ and $\hat{c}_V = c_{V\infty} + (c_{V0} - c_{V\infty})(1 + \tau_1 D)^{-1}$ give the adiabatic index (8) — $\hat{k} = \hat{c}_p/\hat{c}_V$. Having formally written the equation of the adiabat in the form $p\rho^{-\hat{k}} = $ const, we calculate the speed of sound in the mixture of gas and solid particles (7):

$$\hat{a}^2 = \left(\frac{\partial \hat{p}}{\partial \rho}\right)_s = \hat{k}\,\frac{p}{\rho} = k_\infty \left(\frac{p}{\rho}\right)_{\xi s} + \frac{k_0 \left(\dfrac{p}{\rho}\right)_{As} - k_\infty \left(\dfrac{p}{\rho}\right)_{\xi s}}{1 + \tau_V D} = a_\infty^2 + \frac{a_0^2 - a_\infty^2}{1 + \tau_V D}. \tag{22}$$

Replacing D by the eigenvalue $i\omega$, we obtain the relationship first derived by Meixner in acoustic relaxation theory [9]:

$$a^2 = a_\infty^2 + \frac{a_0^2 - a_\infty^2}{1 + i\omega\tau_V}. \tag{23}$$

In conclusion, we note that the formalism used here may prove useful in the analysis of other irreversible processes such as diffusion, phase transitions, chemical reactions, etc.

NOTATION

ξ, relaxation parameter; A, affinity, L, phenomenological coefficient; D, time differentiation operator; τ_x, relaxation time; ω, frequency; p, V, T, pressure, volume, and temperature; k, adiabatic index, τ_0, characteristic time; q, thermal flux density; α, heat-transfer coefficient; C_z, total heat capacity; c_z, c_z', specific mass and volume heat capacities; f, surface; Q, heat; ε, ρ_V, porosity and volume concentration of particles; λ, coefficient of thermal conductivity; $\sigma^{(1)}$, $\beta^{(0)}$, $\beta^{(1)}$, coefficients introduced in [5]; ρ, density; S, entropy; a, speed of sound. Indices: point, time differentiation; ∞, pure gas; 0, equilibrium mixture; s, particle; z = p, V, T, characteristic of thermodynamic process.

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