ON THE THERMODYNAMIC EQUILIBRIUM OF SURFACES OF STRONG DISCONTINUITY

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. I. SKOBELKIN

ON THE THERMODYNAMIC EQUILIBRIUM OF SURFACES OF STRONG DISCONTINUITY

(Presented by Academician S. A. Vekshinskii, 30 VI 1958)

Recently, various variational principles have found application in hydromechanics; for given boundary and initial conditions these principles are equivalent to the equations of motion. For the most general adiabatic motions of a gas (without discontinuities), variational principles and their justification are given in works ([1,2]). However, for motions containing surfaces of strong discontinuity, in addition to a variational principle equivalent to the equations of motion, there must exist a variational principle equivalent to the second law of thermodynamics and expressing the condition of thermodynamic equilibrium of a surface of strong discontinuity. Usually the thermodynamic equilibrium of a physical system is determined from the variational equation $\delta\Phi = 0$ with two or several parameters of the system kept constant. The function Φ, depending on the physical quantities characteristic of the given phenomenon (and subject to variation), is the Gibbs thermodynamic potential ([3]). For example, the position of the vector of spontaneous magnetization of a ferromagnetic crystal is found from the condition $\delta\Phi = 0$, where $\Phi = \mathcal{E} - TS$ is the free energy of the crystal ([4]). In varying the position of the magnetization vector, the specific volume and the temperature remain unchanged.

In hydromechanics, the problem of thermodynamic equilibrium should arise every time one or another variational principle is formulated for describing the motion of a gas. Indeed, infinitesimal deviations from the actual motion, under given boundary and initial conditions, must satisfy not only the variational equation equivalent to the equation of motion, but also the variational equation

$$\Delta Q - T\delta S = 0, \tag{1}$$

equivalent to the second law of thermodynamics for the actual state of a gas in thermodynamic equilibrium. The admissible variations in (1) are the same as the variations determining the actual motion of the gas (the symbol Δ, in contrast to δ, means that ΔQ is not an exact differential). Thus, equation (1) restricts the class of admissible variations.

In hydromechanics, from equation (1) it is generally impossible to obtain Gibbs thermodynamic potentials, since under variation all parameters of the gas change as a result of the motion. Therefore, and also because ΔQ is not an exact differential, the variations Δ and δ in equation (1) must be infinitesimal. In the variational principles known so far and applicable to continuous motion, in particular in the principle of least flow potential ([1],[2]), equation (1) is satisfied identically. For motions with a surface of strong discontinuity, equation (1) is not satisfied identically and gives an additional condition, determining-

constituting the thermodynamic equilibrium of the gas that has passed through the surface of strong discontinuity.

Let us consider the general case of gas motion in the presence of a shock wave or of a sharply defined reaction front separating the initial gas 0 from the burned gas 1. Such a reaction front may be regarded as a particular surface of strong discontinuity. If the gas through which the surface of strong discontinuity propagates is denoted by the index 0, and the gas on the other side of the surface by the index 1, then the laws of conservation of mass, momentum, and energy may be written in the form (⁀5):

$$\rho_0 D = \rho_1 v_{n1}, \tag{2}$$

$$p_0 + \rho_0 D^2 = \rho_1 v_{n1}^2 + p_1, \tag{3}$$

$$E_0(p_0, \tau_0) + p_0\tau_0 + \frac{1}{2}D^2 = E_1(p_1, \tau_1) + p_1\tau_1 + \frac{1}{2}v_{n1}^2, \tag{4}$$

where p is the pressure, ρ the density, $\tau = 1/\rho$, D the velocity of propagation of the surface of strong discontinuity relative to gas 0, v_n the component, normal to the surface, of the velocity of the gas motion relative to the surface, and E the total energy, equal to the sum of the internal energy $\mathcal{E}$ and the "energy of formation," or binding energy, a. For an exothermic reaction the difference $a_0 - a_1 = q$ is the heat of reaction (⁀6), referred to unit mass of gas 0. Eliminating the velocities from (2)–(3) and substituting in (4), we obtain the Hugoniot equation

$$E_0(p_0, \tau_0) - E_1(p_1, \tau_1) = -\frac{1}{2}(\tau_0 - \tau_1)(p_0 + p_1). \tag{5}$$

Suppose that the gas motion is described by a certain variational equation under prescribed boundary conditions and the conditions (2)–(4) on the surface of strong discontinuity (we shall denote it by σ). In particular, if on the surface bounding the flow region ω a distribution of the generalized stream functions ([2,]7) ψ, ϑ is prescribed, and if on σ, which divides the region ω into two regions

ω_1 (isentropic flow) and ω_2 (nonisentropic flow), the conservation laws (2)–(4) are satisfied, then the actual established subsonic flow of an ideal gas satisfies the variational equation

$$\Delta[\psi, \vartheta] \equiv \delta I + \frac{1}{R} \int_{\omega_2} p \, dS \, d\omega - \int_{\sigma} [L]_\sigma \, \delta l \, \overrightarrow{d\sigma} = 0, \tag{6}$$

where

$$I = \int_{\omega} (p + \rho v^2) \, d\omega = \int_{\omega} L \, d\omega$$

is the flow potential (^2) in the discontinuous problem, $\overrightarrow{d\sigma} = \mathbf{n} \, d\sigma$ is the vector surface element, l is an arc of a stream line, $\psi = \text{const}$, $\vartheta = \text{const}$, R is the gas constant, and S is the entropy. In equation (6) the variations are applied to ψ, ϑ under the condition that in ω_1 and ω_2 the Bernoulli equations with unchanged constants are satisfied. The symbol $[L]_\sigma$ denotes the difference of the values of L on the two sides of the surface σ: $[L]_\sigma = L_1 - L_0$. To equation (6) it is necessary to adjoin the variational equation of thermodynamic equilibrium (1), in which ΔQ and δS are determined by the same deviations from the actual state as are contained in (6).

As an example, let us consider the subsonic flow of an ideal gas in a tube in the presence of a flame front propagating with a previously known velocity $D = D(p_0, \tau_0)$ in an isentropic gas with a prescribed Poisson constant. Figure 1 shows the Hugoniot adiabats for a shock wave (OE), a detonation wave (AD), and a weak deflagration (BC).

From equations (2)–(3) for weak deflagration we obtain the Michelson line (^8), along which the thermodynamic process in the reaction zone proceeds:

$$p - p_0 = \frac{D^2}{\tau_0^2} (\tau_0 - \tau).$$

When moving along this straight line to any point of the adiabat BC, one and the same amount of heat q (the heat of reaction) is released. Each state inside the combustion zone satisfies (2)–(4) with variable q. Integrating the equation $dQ = dE + p \, d\tau$ along the Michelson line, we obtain

$$\int dQ = E_0(p_0, \tau_0) - E_1(p_1, \tau_1) + \frac{1}{2} (\tau_0 - \tau_1)(p_0 + p_1),$$

whence, according to (5), $\int dQ = q$. Consequently, for any variation of the state of gas 1, $\Delta Q = \Delta q = 0$, and equation (1) leads to the condition $\delta S_1(p_1, \tau_1) = 0$. A change in the entropy S_1 under variation of the states of gas 1 (such a

Fig. 1

Figure 1: Fig. 1

change is permitted by the constraints) is possible only owing to a change in τ_0 (or p_0) ahead of the flame front. Consequently, for those variations that are allowed by the boundary conditions, by conditions (2)–(4) on σ, and by the other constraints necessary in the corresponding variational principle for the motion of the gas, from $\delta S_1 = 0$ one obtains the differential equation

$$\frac{dS_1(p_1, \tau_1)}{d\tau_0} = 0,$$

which, together with (2)–(4), gives a system of four algebraic equations uniquely determining the parameters $\tau_0, \tau_1, p_1, v_{n1}$ of gases 0 and 1 on the surface of the flame front. Consequently, all parameters of gases 0 and 1 along the flame front are constant, and the motion of the gas behind the flame front is isentropic (vortex-free).

Fig. 1

In some works, in particular [9–12], the established subsonic motion of a gas in the presence of a flame front was hydrodynamically replaced by the motion of two incompressible fluids whose densities changed discontinuously at the flame front. In this case a strong vorticity of the flow behind the flame front was obtained. It follows from what has been proved above that the model of the motion of two incompressible fluids does not satisfy the equation of thermodynamic equilibrium of the flame front (1).

If the gas moves in the presence of a shock wave, then, in order to determine ΔQ for an elementary particle behind the shock wave, it is necessary to investigate nonequilibrium conditions in a transition layer of the order of the mean free path of the gas molecules, in which energy dissipation takes place. The same applies to a detonation wave as well. Determination of ΔQ in these cases is possible only on the basis of the statistical theory of fluctuations in the transition layer.

Moscow State University
named after M. V. Lomonosov

Received
26 V 1958

CITED LITERATURE

1. V. I. Skobelkin, DAN, **108**, No. 5 (1956).

2. V. I. Skobelkin, ZhETF, No. 8 (1956).

3. A. Sommerfeld, *Thermodynamics and Statistical Physics*, IL, 1955.

4. S. V. Vonsovskii, *The Modern Theory of Magnetism*, Moscow, 1953.

5. G. Courant, K. Friedrichs, *Supersonic Flow and Shock Waves*, IL, 1950, pp. 199–227.

6. L. D. Landau, E. M. Lifshitz, *Mechanics of Continuous Media*, Moscow, 1954, pp. 576–605.

7. M. Z. v. Krzywoblocki, *J. Aeronaut. Sci.*, **25**, No. 1 (1958).

8. Ya. B. Zeldovich, *Theory of Shock Waves and Introduction to Gas Dynamics*, Moscow–Leningrad, 1946.

9. A. S. Scurlock, *Mass. Inst. Techn. Meteor. Rep.*, No. 19 (1948).

10. H. S. Tsien, *J. Appl. Mech.*, **18**, No. 2 (1951).

11. G. C. Williams, H. C. Hottel, A. C. Scurlock, *3 Sympos. on Combust. and Flame and Explos. Phenom.*, Baltimore, 1949, p. 21.

12. J. Fabri, R. Siestrunck, C. Fouré, *Rech. Aeronaut.*, No. 25 (1952).

Note: Figure translations are in progress. See original paper for figures.