

We see that allowing for the effect of gradients of transport velocities in a rarefied gas has led to the appearance of additional terms in the dissipation function, each coinciding in structure with the term $T \operatorname{div} V_0$, while the remainder have a more specific form. When there are considerable gradients of transport velocities over the volume elements, the contribution of the terms with coefficients β and γ will be appreciable. Even in the case of an incompressible gas the dissipation energy due to the specific terms can be appreciable. Clearly, one must take account of this kind of variation of the dissipation function, due to volume elements, in the case of gases and liquids which have a complex microstructure.

NOTATION

V , total molecular velocity vector; u, v, w , components of the molecular velocity describing an ordered motion; ξ, η, ζ , components of the molecular velocity describing a random motion; p , pressure; ρ , density; u_0, v_0, w_0 , components of the hydrodynamic volume element; T , temperature; β, γ, R , constants.

LITERATURE CITED

1. A. S. Predvoditelev, *Izv. Akad. Nauk SSSR, Otd. Tekh. Nauk*, No. 4, 545 (1948).
2. A. S. Predvoditelev, in: *Heat and Mass Transfer [in Russian]*, Vol. 3 (edited by A. V. Lykov and B. M. Smol'skii), Gosénergoizdat, Moscow-Leningrad (1963), p. 54.
3. S. Truesdell, *Proc. Roy. Soc.*, **A226**, 59 (1954).
4. S. Truesdell, *J. Math. Pure Appl.*, **37**, 103 (1958).
5. S. V. Vallander, *Dokl. Akad. Nauk SSSR*, **131**, 58 (1960).
6. S. V. Vallander, in: *Proceedings of the All-Union Conference on Theoretical Applied Mechanics [in Russian]*, *Izd. Akad. Nauk SSSR, Moscow-Leningrad* (1962), p. 77.
7. O. A. Ladyzhenskaya, *Mathematical Aspects of the Dynamics of a Viscous Incompressible Fluid [in Russian]*, Nauka, Moscow (1970).
8. J. C. Maxwell, *Phil. Trans.*, **157** (1866).
9. S. Chapman and T. G. Cowling, *Mathematical Theory of Nonuniform Gases*, 3rd ed., Cambridge University Press (1970).
10. V. A. Bubnov, in: *Investigation of Thermohydrodynamic Light Diodes [in Russian]* (edited by A. V. Lykov), Minsk (1970), p. 150.
11. V. A. Bubnov, in: *Energy Transport in Channels [in Russian]* (edited by A. V. Lykov), Nauka i Tekhnika, Minsk (1970), p. 161.
12. J. H. Jeans, *The Dynamical Theory of Gases*, Cambridge University Press (1925).
13. L. Boltzmann, *Lectures on Gas Theory*, University of California Press (1964).

EXERGY REPRESENTATION IN THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

G. P. Yasnikov and V. S. Belousov

UDC 536.70

It is proposed to use the exergy of a system as the thermodynamic Lagrangian. The corresponding variational principle is formulated and its relationship to other variational principles of non-equilibrium thermodynamics is demonstrated.

For constant parameters of the surrounding medium the exergy is a function of the thermodynamic state [1, 2] and in general depends on the generalized coordinates and velocities x_1, \dot{x}_1 . For the case of flux the exergy may be expressed in the form of two alternative forms (Euler and Lagrange) [3]:

$$\delta E = \delta E^{(L)} + \delta K, \quad (1)$$

Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 32, No. 2, pp. 336-341, February, 1977.
Original article submitted February 2, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

$$\delta E^{(L)} = \delta J - T_0 \delta S. \quad (2)$$

For a stationary system

$$\delta E = \delta U - T_0 \delta S + p_0 \delta V. \quad (3)$$

If a certain system is not in equilibrium with the ambient, it may do work

$$\delta L = -\delta E - \delta L^*. \quad (4)$$

This work reaches a maximum when the transition of the system into equilibrium with the ambient is not accompanied by any dissipative processes ($\delta L^* = 0$), i. e., when it is reversible:

$$\delta L_{\max} = -\delta E. \quad (5)$$

The quantity δL_{\max} was used by Landau and Lifshits to construct a theory of thermodynamic fluctuations and to analyze the conditions of stability and a number of dissipative processes [4]. Integrating Eq. (4) with respect to time, we may write down the following variational condition:

$$\int_{t_1}^{t_2} (\delta E + \sum_i \delta L_i) dt = 0. \quad (6)$$

The sum on the left-hand side includes the work of the external fields and the dissipative forces (exergy losses δL^*) and may be represented as follows:

$$\sum_i \delta L_i = \sum_i Q_i \delta x_i. \quad (7)$$

For purely mechanical systems $\delta E^{(L)} = 0$ and the exergy in the Euler form coincides with the kinetic energy of the macroscopic motion of the system (1). In this case the variational condition (5) gives the expression for the Hamilton principle in analytical mechanics [5, 6]:

$$\int_{t_1}^{t_2} (\delta K + \sum_i \delta L_i) dt = 0, \quad (8)$$

from which the Lagrange equations follow. For a system in external conservative fields the integrand in (8) equals the Lagrange function $\mathcal{L} = K - \Pi$.

For a stationary thermodynamic system without dissipation ($\delta L^* = 0$) Eq. (6) takes the form

$$\int_{t_1}^{t_2} \delta E dt = 0. \quad (9)$$

Assuming that $E = E(S, V)$, $U = U(S, V)$ and allowing for (3), we may evaluate δE :

$$\delta E = \left(\frac{\partial U}{\partial S} \right)_V \delta S + \left(\frac{\partial U}{\partial V} \right)_S \delta V - T_0 \delta S + p_0 \delta V = (T - T_0) \delta S + (p_0 - p) \delta V. \quad (10)$$

Since δE does not depend on the time, while the integration range $t_1 - t_2$ is arbitrary, Eqs. (9) and (10) yield the conditions of thermodynamic equilibrium of the system: $p = p_0$, $T = T_0$. It is easy to show [4] that $\delta^2 E > 0$ and that in a state of equilibrium the function (3) has a minimum.

The deviation of the entropy of the system and the ambient from the maximum value at equilibrium is [4]

$$\Delta S = \frac{L_{\max}}{T_0} = -\frac{\Delta E}{T_0}. \quad (11)$$

Defining the thermodynamic forces in the usual way [7], with the aid of Eq. (11) we may express these in terms of the exergy of the system:

$$X_i = -\frac{\partial \Delta S}{\partial x_i} = -\frac{1}{T_0} \frac{\partial L_{\max}}{\partial x_i} = \frac{1}{T_0} \frac{\partial E}{\partial x_i}. \quad (12)$$

Thus, the derivative

$$\frac{\partial E}{\partial x_i} = T_0 X_i = Q_i \quad (13)$$

defines certain thermodynamic forces in the exergy representation. By varying (11) at constant ambient temperature

$$\delta E = \delta(\Delta E) = -T_0 \delta \Delta S \quad (14)$$

and substituting δE into the variational condition (6), we obtain

$$\int_{t_1}^{t_2} \left[\delta(-\Delta S) + \sum_i X_i \delta x_i \right] dt = 0. \quad (15)$$

Equation (15) represents the variational principle of Bakhareva [8]. After giving detailed consideration to the mechanical analogs of nonequilibrium thermodynamics [9], Bakhareva chose $-\Delta S$ as the thermodynamic Lagrangian.

Since $\Delta S = f(x_i)$, the variational principle (15) only describes inertialess processes. There is no analog to the kinetic energy in this case. In this sense the construction of (6) is more general, since the exergy of the system may include the kinetic energy, so that in principle inertial effects may be taken into account. Thus, the variational condition (6) may be used to describe thermomechanical processes.

By way of example, let us consider the motion of solid particles in a field of gravitational forces and a resistant medium at constant temperature.

The system of Euler-Lagrange equations for the variational condition (6) with due allowance for (7) takes the form

$$\frac{d}{dt} \frac{\partial E}{\partial \dot{x}_i} - \frac{\partial E}{\partial x_i} = Q_i. \quad (16)$$

We shall consider the medium and the particle as a single adiabatically insulated system. In accordance with (1) the exergy of this system is

$$E = E^{(L)}(x_i) + K(\dot{x}_i). \quad (17)$$

The gravitational force acting on each particle may be represented as follows:

$$Q_i = -\frac{\partial \Pi}{\partial x_i}. \quad (18)$$

Substituting (17) and (18) into (16), we obtain

$$\frac{d}{dt} \frac{\partial K}{\partial \dot{x}_i} + \frac{\partial \Pi}{\partial x_i} = Q_i^*, \quad (19)$$

where $\partial E^{(L)}/\partial x_i = Q_i^*$ in accordance with (13) constitutes the resistive force of the ambient. Introducing the Lagrangian $\mathcal{L} = K - \Pi$ into (19), we obtain the Lagrange equation in the ordinary form [5, 6]:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = Q_i^*. \quad (20)$$

It was shown in [9] that for the adiabatic system

$$\frac{\partial \Delta S}{\partial x_k} = \frac{\partial \Phi}{\partial x_k}, \quad (21)$$

where $\Phi(\dot{x}_k)$ is the scattering function or the dissipative function in the entropy representation.

Multiplying both sides of (21) by T_0 and allowing for (12)-(14), we obtain

$$\frac{\partial E}{\partial x_i} = -T_0 \frac{\partial \Delta S}{\partial x_i} = -T_0 \frac{\partial \Phi}{\partial x_i} = -\frac{\partial f}{\partial x_i} = Q_i^* \quad (22)$$

($f = \Phi T_0$). Substituting (22) into (20), we obtain the Lagrange equation for the particles in the form [4]

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} - \frac{\partial \mathcal{L}}{\partial x_i} = -\frac{\partial f}{\partial x_i}. \quad (23)$$

In order to write down the variational equation analogous to (6) for continuous systems, the parameters of which form corresponding scalar, vector, and tensor fields, we differentiate (4) with respect to time, assuming that there is no distinct external object of work ($\delta L = 0$):

$$\delta \dot{E} + \delta \dot{L}^* = 0. \quad (24)$$

Remembering that

$$\dot{E} = \int_V \rho \dot{e} dV, \quad (25)$$

$$\dot{L}^* = \int_V f dV, \quad (26)$$

we put (24) in the form

$$\delta \int_V (\rho \dot{e} + f) dV = 0. \quad (27)$$

By way of illustration, let us apply the variational condition (27) to the description of heat conduction in a solid. We write down the balance equation for the exergy:

$$\rho \dot{e} = -\operatorname{div} \vec{J}_e - \sigma_e. \quad (28)$$

The sink σ_e , the dissipative function f , and the flux \vec{J}_e with due allowance for [2, 7] may be expressed in the form

$$\sigma_e = T_0 \vec{J}_q \cdot \vec{\nabla} \frac{1}{T}; \quad f = \frac{1}{2} T_0 L_{qq} \left(\vec{\nabla} \frac{1}{T} \right)^2; \quad \vec{J}_e = \left(1 - \frac{T_0}{T} \right) \vec{J}_q. \quad (29)$$

We set down the identity

$$\operatorname{div} \vec{J}_e = \operatorname{div} \left(1 - \frac{T_0}{T} \right) \vec{J}_q = -T_0 \vec{J}_q \cdot \vec{\nabla} \frac{1}{T} + \vec{\nabla} \cdot \vec{J}_q - \frac{T_0}{T} \vec{\nabla} \cdot \vec{J}_q. \quad (30)$$

Substituting σ_e and \vec{J}_e from (29) into (28) and then (28) and f from (29) into (27) and using the Gauss—Ostrogradskii equation, we obtain

$$\delta \left\{ \int_V \left[\frac{T_0}{T} \vec{\nabla} \cdot \vec{J}_q + \frac{1}{2} T_0 L_{qq} \left(\vec{\nabla} \frac{1}{T} \right)^2 \right] dV - \oint_S \vec{J}_q \cdot d\vec{S} \right\} = 0. \quad (31)$$

In (31) we shall only vary with respect to $1/T$, considering that $\delta \vec{J}_q = 0$ and $1/T$ does not vary along the boundary. Expressing the $\vec{\nabla} \cdot \vec{J}_q$ in (31) on the basis of the first law of thermodynamics

$$\rho c_v \frac{\partial T}{\partial t} = -\vec{\nabla} \cdot \vec{J}_q \quad (32)$$

and carrying out the variation operation, we obtain

$$T_0 \int_V \left[\rho c_v \frac{\partial T}{\partial t} + \vec{\nabla} \cdot \left(L_{qq} \vec{\nabla} \frac{1}{T} \right) \right] \delta \left(\frac{1}{T} \right) dV = 0. \quad (33)$$

It follows from (33) that

$$\rho c_v \frac{\partial T}{\partial t} = -\vec{\nabla} \cdot L_{qq} \vec{\nabla} \frac{1}{T} \quad (34)$$

or in the usual representation $\lambda = L_{qq} T^{-2}$

$$\rho c_v \frac{\partial T}{\partial t} = \vec{\nabla} \cdot (\lambda \vec{\nabla} T).$$

From the variational condition (27) it is easy to transform to the Gyarmatis variational principle [7]. For this we differentiate (27) with respect to the ambient temperature:

$$\delta \int_V \left[\frac{\partial}{\partial T_0} \rho \dot{e} + \frac{\partial f}{\partial T_0} \right] dV = 0. \quad (35)$$

From (3)

$$\frac{\partial \rho \dot{e}}{\partial T_0} = -\rho s. \quad (36)$$

The derivative $\partial f / \partial T_0$ is equal to the scattering function [7]

$$\frac{\partial f}{\partial T_0} = \Phi(\vec{X}, \vec{X}), \quad (37)$$

since $f = T_0 \Phi(\vec{X}, \vec{X})$. From the entropy balance equation we may write $\rho \dot{s}$ as

$$\rho \dot{s} = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s. \quad (38)$$

Substituting (36), (37), and (38) into (35) and using the Gauss—Ostrogradskii theorem, we obtain

$$\delta \left\{ \int_V [\sigma_s - \Phi] dV - \oint_S \vec{J}_s d\vec{S} \right\} = 0. \quad (39)$$

Variation at constant fluxes gives the Gyarmatis principle [7] in the form

$$\delta \int_V [\sigma_s - \Phi]_{\vec{J}_s} dV = 0 \quad (40)$$

or, if we substitute (36) and (37) into (35),

$$\delta \int_V [\rho \dot{s} - \Phi] dV = 0. \quad (41)$$

In conclusion, we note that in [10], Bakhareva made a detailed study of the analytical relationship between the variational principle (15) and other variational principles of nonequilibrium thermodynamics. Since we may transform from (6) to (15), it is clear that the exergy representation also has a connection with the other variational principles of Onsager [7], Biot [11], and Siegler [12]. Finally, in [13, 14] irreversible processes are described by means of the Gibbs potential, the variation of which coincides with the variation of the exergy provided that the temperatures and pressures of the system and medium are equal.

NOTATION

$E, E(L)$, total exergies of the system in the Euler and Lagrange forms, respectively; L, L_{\max} , work done by the system and maximum work of the system; U, I, S, V , total internal energy, enthalpy, entropy, and volume of the system; e, s , specific exergy and entropy; K, Π , kinetic and potential energies; \mathcal{L} , Lagrangian; L^* , exergy losses; Q, X , generalized forces in the exergy and entropy representations; Φ, f , dissipative function or scattering function; $\vec{J}_q, \vec{J}_e, \vec{J}_s$, flows of heat, exergy, and entropy; σ_e, σ_s , specific powers of the exergy and entropy sources; L_{qq} , phenomenological coefficient; λ , thermal conductivity; c_v , specific heat of the system at constant volume; ρ , density; \dot{x}_i, x_i , generalized velocities and coordinates; t , time; p_0, T_0 , ambient pressure and temperature.

LITERATURE CITED

1. Ya. Shargut and R. Petela, Exergy [in Russian], *Énergiya*, Moscow (1968).
2. V. M. Brodyanskii, Exergy Method of Thermodynamic Analysis [in Russian], *Énergiya*, Moscow (1973).
3. G. P. Yasnikov, *Izv. Vyssh. Uchebn. Zaved., Energ.*, No. 9 (1975).
4. L. D. Landau and E. M. Lifshits, *Statistical Physics*, 2nd ed., Addison-Wesley (1969).
5. L. A. Pars, *Treatise on Analytical Dynamics*, Wiley (1965).
6. C. Lanczos, *Variational Principles of Mechanics*, 3rd ed., University of Toronto Press (1966).
7. I. Gyarmatis, *Nonequilibrium Thermodynamics: Field Theory and Variational Principles*, Springer-Verlag (1970).
8. I. F. Bakhareva, *Zh. Fiz. Khim.*, 42, No. 10 (1968).
9. I. F. Bakhareva, *Zh. Fiz. Khim.*, 41, No. 7 (1967).
10. I. F. Bakhareva, *Inzh.-Fiz. Zh.*, 20, No. 6 (1971).
11. M. A. Biot, *Phys. Rev.*, 97, 1463 (1955).
12. H. Siegler, *Extremal Principles in the Thermodynamics of Irreversible Processes and the Mechanics of Continuous Media* [Russian translation], Mir, Moscow (1966).
13. B. S. Sadykov, *Zh. Fiz. Khim.*, 43, No. 3 (1969).
14. B. S. Sadykov, *Zh. Fiz. Khim.*, 47, No. 3 (1973).