

G. P. Yasnikov, V. S. Belousov,  
and A. A. Morilov

UDC 536.70

It is proposed to use the exergy of a thermodynamic system to analyze relaxation processes. A relation between the relaxation time and the exergy of a thermodynamic system is obtained.

Systems submerged in a thermostat (environment) and interacting with it must be considered in solving a whole series of applied thermodynamics problems. The system and thermostat are here not in equilibrium. Naturally, a thermodynamic potential of more general type than the free energy or isobaric Gibbs potential is necessary for such systems. Indeed, Landau and Lifshits [1] used the exergy to describe fluctuations and to investigate stability and dissipative processes.

The exergy can be used as a thermodynamic Lagrangian in the formulation of variational principles for the thermodynamics of irreversible processes. Such an approach [2, 3] permits bypassing a number of difficulties which occur in the utilization of other thermodynamic functions as a Lagrangian.

The application of the relaxational formalism of the thermodynamics of irreversible processes [4, 5] to disperse systems permitted the description of a number of processes such as acoustic relaxation, compression of a dusty gas in a compressor, and heat conduction of suspensions [6, 7], from a single viewpoint. Exergy can also be used to extend the relaxation formalism of nonequilibrium thermodynamics to the case of a system in a thermostat. The present paper is devoted to a clarification of this question.

Let us consider the exergy of a fixed system

$$dE = dU - T_0 dS + p_0 dV \quad (1)$$

and the exergy of a stream of material in a system of the center of mass of the extracted element

$$dE_f = dH - T_0 dS. \quad (2)$$

For systems in which the relaxation process characterized by the parameter  $\xi$  proceeds, the fundamental Gibbs equation is valid [8]

$$dU = T dS - p dV - A d\xi, \quad (3)$$

$$dH = T dS + V dp - A d\xi. \quad (4)$$

If several relaxation processes proceed in the system, then the quantities  $A$  and  $\xi$  can be interpreted as vectors with the components  $A_1, \dots, A_n, \xi_1, \dots, \xi_n$ . Moreover, since a thermodynamic analysis of a chemical reaction is analogous to the description of relaxation processes, (1)-(4) and all the subsequent results can be used for systems in which chemical reactions proceed. Eliminating  $dU$  in (1) by using (3) and  $dH$  in (2) by using (4), we have

$$dE = (T - T_0) dS - (p - p_0) dV - A d\xi, \quad (5)$$

$$dE_f = (T - T_0) dS + V dp - A d\xi. \quad (6)$$

Taking into account that the differentials  $dE(S, V, \xi)$  and  $dE_f(S, p, \xi)$  are total, we obtain

$$\left( \frac{\partial E}{\partial S} \right)_{V, \xi} = \left( \frac{\partial E_f}{\partial S} \right)_{p, \xi} = T - T_0; \quad \left( \frac{\partial E}{\partial V} \right)_{S, \xi} = p_0 - p; \quad (7)$$

$$\left( \frac{\partial E_f}{\partial p} \right)_{S, \xi} = V; \quad \left( \frac{\partial E}{\partial \xi} \right)_{S, V} = \left( \frac{\partial E_f}{\partial \xi} \right)_{S, p} = -A.$$

Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 37, No. 3, pp. 513-517, September, 1979. Original article submitted November 21, 1978.

If we select  $U, V, \xi$  as independent variables defining  $E$ , and  $H, p, \xi$  for  $E_f$ , then there follows from (1)-(4)

$$dE = \tau^{(e)}dU + [p_0 - (1 - \tau^{(e)}) p] dV - (1 - \tau^{(e)}) Ad\xi, \quad (8)$$

$$dE_f = \tau^{(e)}dH + (1 - \tau^{(e)}) Vdp - (1 - \tau^{(e)}) Ad\xi, \quad (9)$$

where  $\tau^{(e)} = 1 - (T_0/T)$ . From (8) and (9) we find

$$\begin{aligned} \left(\frac{\partial E}{\partial U}\right)_{V,\xi} &= \left(\frac{\partial E_f}{\partial H}\right)_{p,\xi} = \tau^{(e)}; & \left(\frac{\partial E}{\partial V}\right)_{U,\xi} &= p_0 - (1 - \tau^{(e)}) p; \\ \left(\frac{\partial E_f}{\partial p}\right)_{H,\xi} &= (1 - \tau^{(e)}) V; & \left(\frac{\partial E}{\partial \xi}\right)_{U,V} &= \left(\frac{\partial E_f}{\partial \xi}\right)_{H,p} = -(1 - \tau^{(e)}) A. \end{aligned} \quad (10)$$

Substituting the total differentials  $dU(T, V, \xi)$  and  $dH(T, p, \xi)$  in (8) and (9), we obtain

$$dE = C_V \tau^{(e)} dT + \tau^{(e)} \left[ (T - T_0) \left(\frac{\partial p}{\partial T}\right)_{V,\xi} + (p_0 - p) \right] dV + \left[ \tau^{(e)} \left(\frac{\partial U}{\partial \xi}\right)_{T,V} - (1 - \tau^{(e)}) A \right] d\xi, \quad (11)$$

$$dE_f = \tau^{(e)} C_p dT + \left[ V + (T_0 - T) \left(\frac{\partial V}{\partial T}\right)_{p,\xi} \right] dp + \left[ \tau^{(e)} \left(\frac{\partial H}{\partial \xi}\right)_{p,T} - (1 - \tau^{(e)}) A \right] d\xi. \quad (12)$$

For the derivatives  $(\partial U/\partial \xi)_{T,V}$  and  $(\partial H/\partial \xi)_{T,p}$  we can write [8]

$$\left(\frac{\partial U}{\partial \xi}\right)_{T,V} = \left(\frac{\partial F}{\partial \xi}\right)_{T,V} + T \left(\frac{\partial S}{\partial \xi}\right)_{T,V} = - \left[ T \left(\frac{\partial A}{\partial T}\right)_{V,\xi} + A \right], \quad (13)$$

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,p} = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} + T \left(\frac{\partial S}{\partial \xi}\right)_{T,p} = T \left(\frac{\partial A}{\partial T}\right)_{p,\xi} - A. \quad (14)$$

Taking (13) and (14) into account, (11) and (12) become

$$dE = \tau^{(e)} C_V dT + \left[ (T - T_0) \left(\frac{\partial p}{\partial T}\right)_{V,\xi} + (p_0 - p) \right] dV + \left[ (T_0 - T) \left(\frac{\partial A}{\partial T}\right)_{V,\xi} - A \right] d\xi, \quad (15)$$

$$dE_f = \tau^{(e)} C_p dT + \left[ V + (T_0 - T) \left(\frac{\partial V}{\partial T}\right)_{p,\xi} \right] dp + \left[ (T - T_0) \left(\frac{\partial A}{\partial T}\right)_{p,\xi} - A \right] d\xi, \quad (16)$$

from which follows

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_{V,\xi} &= \tau^{(e)} C_V; & \left(\frac{\partial E}{\partial V}\right)_{T,\xi} &= (T - T_0) \left(\frac{\partial p}{\partial T}\right)_{V,\xi} + (p_0 - p); \\ \left(\frac{\partial E_f}{\partial T}\right)_{p,\xi} &= \tau^{(e)} C_p; & \left(\frac{\partial E_f}{\partial p}\right)_{T,\xi} &= \left[ V - (T - T_0) \left(\frac{\partial V}{\partial T}\right)_{p,\xi} \right]; \\ \left(\frac{\partial E}{\partial \xi}\right)_{T,V} &= (T_0 - T) \left(\frac{\partial A}{\partial T}\right)_{V,\xi} - A; \\ \left(\frac{\partial E_f}{\partial \xi}\right)_{T,p} &= (T - T_0) \left(\frac{\partial A}{\partial T}\right)_{p,\xi} - A. \end{aligned} \quad (17)$$

If the differential of the entropy  $S = S(E, V, \xi)$  is expressed from (5) and (6), then the expression

$$A = (T - T_0) \left(\frac{\partial S}{\partial \xi}\right)_{E,V} = (T - T_0) \left(\frac{\partial S}{\partial \xi}\right)_{E_f,p} \quad (18)$$

can be obtained for the affinity of the process. The phenomenological law

$$\frac{d\xi}{dt} = LA \quad (19)$$

can be written for the velocity of the relaxation process, where the affinity  $A$  is a function of the state  $A(x, y, \xi)$ , and  $x$  and  $y$  are parameters of this state. Expanding  $A$  in a series for unchanged  $x$  and  $y$

$$A = A_{\text{equi}} + \left( \frac{\partial A}{\partial \xi} \right)_{x, y} \Delta \xi + O(\Delta \xi^2) \quad (20)$$

and taking into account that  $\Delta_{\text{equi}} = 0$  in an equilibrium state, we rewrite (19) in the form

$$\frac{d\xi}{dt} = - \frac{\Delta \xi}{\tau_{xy}} = \frac{\Delta \xi}{\left[ L \left( \frac{\partial A}{\partial \xi} \right)_{x, y} \right]^{-1}} \quad (21)$$

Hence

$$\tau_{xy} = - \left[ L \left( \frac{\partial A}{\partial \xi} \right)_{x, y} \right]^{-1} \quad (22)$$

Giving the values  $(S, V)$ ,  $(S, p)$ ,  $(U, V)$ ,  $(H, p)$  successively to  $x$  and  $y$ , we express the relaxation time in terms of the exergy by using (7) and (10)

$$\tau_{SV} = \left[ L \left( \frac{\partial^2 E}{\partial \xi^2} \right)_{S, V} \right]^{-1}; \quad \tau_{Sp} = \left[ L \left( \frac{\partial^2 E}{\partial \xi^2} \right)_{S, p} \right]^{-1} \quad (23)$$

Using (18), we obtain the relaxation time for constant  $E, V$  and  $E_f, p$ :

$$\tau_{EV} = - \left[ L (T - T_0) \left( \frac{\partial^2 S}{\partial \xi^2} \right)_{E, V} \right]^{-1}; \quad (24)$$

$$\tau_{E_f, p} = - \left[ L (T - T_0) \left( \frac{\partial^2 S}{\partial \xi^2} \right)_{E_f, p} \right]^{-1}.$$

The relaxation time for constant  $V, T$  and  $p, T$  can be found from (22) and (17) with (13) and (14) taken into account:

$$\tau_{VT} = \left\{ L \left[ \left( \frac{\partial^2 E}{\partial \xi^2} \right)_{T, V} - (T - T_0) \left( \frac{\partial^2 S}{\partial \xi^2} \right)_{T, V} \right] \right\}^{-1}; \quad (25)$$

$$\tau_{pT} = \left\{ L \left[ \left( \frac{\partial^2 E_f}{\partial \xi^2} \right)_{T, p} - (T - T_0) \left( \frac{\partial^2 S}{\partial \xi^2} \right)_{T, p} \right] \right\}^{-1}.$$

The partial derivatives in all the expressions for the relaxation time are evaluated in the equilibrium state [8]. Using different relationships between the thermodynamic derivatives, we can set up a relationship between different relaxation times.

The very same formalism can be used for complex thermodynamic systems. However, in this case the generalized enthalpy [9]

$$H^* = \begin{pmatrix} H + \vec{B} \cdot \vec{m} \\ H + \vec{E} \cdot \vec{p} \\ H + Mgz \end{pmatrix} \quad (26)$$

must be used in place of  $H$ . By using (8), (9) and the equations of the first law of thermodynamics in the form

$$dQ = dU + pdV, \quad (27)$$

$$dQ = dH - Vdp, \quad (28)$$

an expression can be obtained for the useful work performed by the system and the flux of material in which the relaxation processes proceed:

$$dL_V = (p - p_0) dV = dE^{(Q)} - dE - T_0 \frac{A}{T} d\xi, \quad (29)$$

$$dL' = -Vdp = dE^{(Q)} - dE_f - T_0 \frac{A}{T} d\xi, \quad (30)$$

where  $dE^{(Q)} = \tau^{(e)}dQ$  is the thermal exergy. The last terms in the right-hand sides of (29) and (30) express the exergetic losses caused by irreversibility of the processes.

Relaxation processes can be taken into account in the local exergy balance equations [10] for a continuous nonequilibrium system. If the system is closed or in equilibrium with the medium for constant pressure and temperature, then the relationships obtained yield the well-known classical results [4, 5, 8].

And finally, we note that relations (29) and (30) can be used for an exergetic analysis of nonstationary processes. These problems are of practical interest but the methods of their solution have not been developed at this time, and we can only refer to Ya. Shargut and R. Petela who indicated the possibility of using the thermodynamics of irreversible processes here.

#### NOTATION

$E$	is the physical exergy;
$E_f$	is the stream physical exergy;
$U$	is the internal energy;
$H$	is the enthalpy;
$S$	is the entropy;
$T$	is the temperature;
$p$	is the pressure;
$V$	is the volume;
$A$	is the affinity of the relaxation process;
$\xi$	is the relaxation parameter;
$\tau^{(e)}$	is the exergetic temperature;
$L$	is the phenomenological coefficient;
$\tau_{xy}$	is the relaxation time under the condition that the parameters $x$ and $y = \text{const}$ ;
$E^{(Q)}$	is the thermal exergy;
$L_V, L'$	are the useful work;
$\vec{B}, \vec{m}$	are the magnetic field induction and magnetic moment;
$\vec{E}, \vec{p}$	are the electric field intensity and polarization;
$M$	is the mass;
$z$	is the center of gravity coordinate;
$g$	is the free-fall acceleration;
	the subscript 0 refers to the parameters of the medium.

#### LITERATURE CITED

1. L. D. Landau and E. M. Lifshits, *Statistical Physics* [in Russian], Nauka, Moscow (1964).
2. M. A. Biot, *Bull. cl. sci. Acad. R. Belg.*, 61, No. 1 (1975).
3. G. P. Yasnikov and V. S. Belousov, *Inzh.-Fiz. Zh.*, 32, No. 2 (1977).
4. H. E. Múser and J. Peterson, *Fortschr. Phys.*, 19 (1971).
5. J. Meixner, *Koll. Z.*, 134, No. 1 (1953).
6. G. P. Yasnikov and V. S. Belousov, *Inzh.-Fiz. Zh.*, 34, No. 6 (1978).
7. G. P. Yasnikov, in: *Heat and Mass Transfer and Nonequilibrium Thermodynamics of Disperse Systems* [in Russian], Ural Polytech. Inst., Sverdlovsk (1974).
8. R. Haase, *Thermodynamics of Irreversible Processes*, Addison-Wesley (1968).
9. G. P. Yasnikov, *Izv. Vyssh. Uchebn. Zaved., Energ.*, No. 9 (1975).
10. G. P. Yasnikov and V. S. Belousov, *Inzh.-Fiz. Zh.*, 32, No. 1 (1977).
11. Ya. Shargut and R. Petela, *Exergy* [in Russian], Nauka, Moscow (1968).