

GENERALIZATION OF ONSAGER'S PRINCIPLE  
AND ITS APPLICATION

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A principle is introduced to the thermodynamics of irreversible processes which generalizes the well-known Onsager principle. On the basis of this principle, an equation of heat conduction is derived with a finite velocity of heat propagation, and a system of equations of coupled thermoelasticity is set up.

The theory of transfer processes embraces diverse phenomena: heat conduction, electric current conduction, also diffusion and absorption of sound. Transfer occurs in systems which are not in a state of thermodynamic equilibrium. The rate of a transfer process determines the change in the physical potential. The choice of potential is based on the following premise: if the location of extraneous bodies around a system is fixed, then with time the physical system will eventually make a transition to equilibrium.

One of the basic principles in the thermodynamics of irreversible processes is Onsager's principle: fluxes are linear functions of thermodynamic forces

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1, 2, 3, \dots, n). \quad (1)$$

The matrix of the  $L_{ik}$  coefficients is symmetric, i.e.,  $L_{ik} = L_{ki}$ . The symmetry of this matrix is a consequence of reversibility on the microscopic scale. An essential deficiency of this stated principle and of the phenomenological laws derived therefrom is, in the author's view, that they ignore the history prior to the action of thermodynamic forces, i.e., the inertial characteristics of the energy carriers.

This was pointed out first by Lykov [1, 2], who noted that the phenomenological coefficients in (1) must not necessarily be considered constant in the case of transient transfer processes.

In order to remove the said deficiency, this author proposes to formulate Onsager's principle differently: fluxes and thermodynamic forces are related as follows:

$$J_i = \sum_{k=1}^n L_{ik} \int_0^t X_k K(t-t') dt', \quad (2)$$

where  $K(t-t')$  is the relaxation kernel. The matrix of the  $L_{ik}$  coefficients is symmetric. Then the rate of energy increase can be expressed as

$$\sigma = \sum_i \sum_k \dot{X}_i L_{ik} \int_0^t X_k K(t-t') dt' > 0. \quad (3)$$

If the relaxation kernel, equal to the  $\delta$ -function, is represented as  $K(t-t') = \delta(t-t')$ , then (2) will yield the well-known Onsager principle:

$$J_i = \sum_{k=1}^n L_{ik} X_k.$$

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When

$$K(t-t') = \frac{1}{\tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right), \quad (4)$$

with  $\tau_r$  denoting the relaxation time, then (2) yields

$$q_i = L_{ih} \int_0^t \nabla T \frac{1}{\tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right) dt', \quad (5)$$

where  $q_i$  denotes the thermal flux and  $\nabla T$  denotes the temperature gradient. From (5) we obtain the equation of heat transfer first derived by Lykov in [2]:

$$q + \tau_r \frac{\partial q}{\partial t} = -\lambda_{\odot} \nabla T. \quad (6)$$

Here  $\lambda_{\odot}$  denotes the thermal conductivity. We will write Eq. (5) in a different form now:

$$q_i = L_{ih} \left\{ \nabla T \left[ 1 - \exp\left(-\frac{t}{\tau_r}\right) \right] - \int_0^t \frac{\partial}{\partial t'} (\nabla T) \exp\left(-\frac{t-t'}{\tau_r}\right) dt' \right\}. \quad (7)$$

If the thermodynamic forces vary only slightly with time, then (7) may be expressed as

$$q_i = L_{ih} \nabla T \left[ 1 - \exp\left(-\frac{t}{\tau_r}\right) \right] \quad (8)$$

or as the following expression for the thermal flux:

$$q_i = \lambda_{\odot} \nabla T \left[ 1 - \exp\left(-\frac{t}{\tau_r}\right) \right]. \quad (9)$$

When  $\partial q/\partial t = 0$ , we have Fourier's law of heat conduction. Using (6), we can now derive the hyperbolic equation of heat conduction:

$$\nabla^2 T = \frac{1}{a} \frac{\partial T}{\partial t} + \frac{1}{v_r^2} \frac{\partial^2 T}{\partial t^2}, \quad (10)$$

with the thermal diffusivity  $a$  and with  $v_r = \sqrt{a/\tau_r}$ . We will now derive, approximately, the equation of heat transfer in form (5) for a neutral gas, based on the fundamental equation of kinetics: the Boltzmann equation. The linearized Boltzmann equation for a neutral gas is

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = \left[ \frac{\partial f}{\partial t} \right]_c. \quad (11)$$

Here  $f$  is the distribution function of particles and  $[\partial f/\partial t]_c$  is the collision integral. The linearization is effected by replacing the exact collision integral with

$$\left[ \frac{\partial f}{\partial t} \right]_c = -\frac{f - f_0}{\tau_r}, \quad (12)$$

where  $f_0$  denotes the distribution function at equilibrium. Substitution (12) is obviously permissible, provided that the change in the energy of particles during collisions is small and that the collisions result in a random distribution of velocities. We will express this distribution as follows:

$$f = f_0 + vX(r, t), \quad (13)$$

where function  $X$  characterizes the deviation of the system from equilibrium and this deviation is assumed small. Inserting (13) into (11), with (12) taken into account, yields

$$\frac{\partial X}{\partial t} + \frac{X}{\tau_r} = -\nabla f_0. \quad (14)$$

In (14) we have disregarded the terms of second-order smallness with respect to  $X$ . As  $f_0$  we adopt Maxwell's equilibrium distribution function

$$f_0 = \exp\left(-\frac{\varepsilon}{T}\right), \quad (15)$$

and have then

$$\nabla f_0 = -\varepsilon \frac{\partial f_0}{\partial \varepsilon} \nabla \ln T. \quad (16)$$

Inserting (16) into (14) yields

$$\frac{\partial X}{\partial t} + \frac{X}{\tau_r} = \varepsilon \frac{\partial f_0}{\partial \varepsilon} \nabla \ln T. \quad (17)$$

Having determined  $X$  from (17), we may now write for the distribution function

$$f = f_0 + v \int_0^t \varepsilon \tau_r \frac{\partial f_0}{\partial \varepsilon} \frac{\nabla \ln T}{\tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right) dt'. \quad (18)$$

Let us next derive the distribution function for a neutral gas with a specified temperature gradient. We calculate the thermal flux from the distribution function (18). We obtain

$$q = \frac{1}{4\pi^3} \int \varepsilon v f d^3v. \quad (19)$$

We insert (18) into (19):

$$q = \frac{1}{4\pi^3} \int \varepsilon v \left[ f_0 + v \int_0^t \varepsilon \tau_r \frac{\partial f_0}{\partial \varepsilon} \frac{\nabla \ln T}{\tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right) dt' \right] d^3v \quad (20)$$

and then have

$$q = \int_0^t \frac{\nabla T}{T \tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right) dt' \frac{1}{4\pi^3} \int \varepsilon^2 v^2 \tau_r \frac{\partial f_0}{\partial \varepsilon} d^3v. \quad (21)$$

Integrating over the velocity space results in  $\int \varepsilon v f_0 d^3v = 0$  because, for a symmetric equilibrium function, to any value of  $+v$  there corresponds a value  $-v$  and the total integral vanishes. Expression  $(1/4\pi^3) \int \varepsilon^2 v^2 \tau_r (\partial f_0 / \partial \varepsilon) d^3v$  represents the coefficient  $L_2$ , so that (21) may be represented as

$$q = L_2 \int_0^t \nabla T \frac{1}{T \tau_r} \exp\left(-\frac{t-t'}{\tau_r}\right) dt' \quad (22)$$

and

$$q + \tau_r \frac{\partial q}{\partial t} = -\lambda_\Theta \nabla T, \quad \lambda_\Theta = \frac{L_2}{T},$$

which corresponds to (5).

The equation of state for an elastic medium with small deformations is

$$\sigma_{ik} = 2\mu l_{ik} + \lambda j_1 \delta_{ik} + \alpha_T \left( \lambda + \frac{2\mu}{3} \right) (T - T_0) \delta_{ik}. \quad (23)$$

Here  $\sigma_{ik}$  is the stress tensor;  $\lambda$  and  $\mu$  are the Lamé constants;  $\alpha_T$  denotes the linear thermal expansivity;  $l_{ik}$  is the strain tensor; and  $j_1$  is the first invariant of the strain tensor.

The amount of heat absorbed in a unit volume is

$$dQ = C_e T + T_0 \left( \lambda + \frac{2\mu}{3} \right) \alpha_T j_1, \quad (24)$$

with  $C_e$  denoting the specific heat at constant strain. For the heat conduction process we have

$$\frac{\partial Q}{\partial t} = -\operatorname{div} \mathbf{q}. \quad (25)$$

On the basis of (6), one can obtain the general equation of heat conduction

$$\frac{1}{a} \frac{\partial T}{\partial t} + \frac{1}{v_T^2} \frac{\partial^2 T}{\partial t^2} - \nabla^2 T - \frac{T_0 \alpha_T \left( \lambda + \frac{2\mu}{3} \right)}{\lambda_0} \left( \frac{\partial j_1}{\partial t} + \tau_T \frac{\partial^2 j_1}{\partial t^2} \right) = 0. \quad (26)$$

Equation (26) together with the equation of motion

$$\sigma_{ik,k} + F_i = \rho \frac{\partial^2 u_i}{\partial t^2} \quad (27)$$

form a system which describes the process of coupled thermoelasticity with a finite velocity of heat propagation. If the body forces, the surface forces, and the heat sources vary with time slowly, then one may delete the inertia term from the equations of motion and the problem of coupled thermoelasticity may be considered quasistatic.

The fundamental equations of quasistatic coupled thermoelasticity are

$$\operatorname{grad} [(\lambda + 2\mu) \nabla^2 \Phi - \gamma T] = 0, \quad (28)$$

$$\nabla^2 T - \frac{1}{a} \frac{\partial T}{\partial t} - \frac{1}{v_T^2} \frac{\partial^2 T}{\partial t^2} - \eta \left( \frac{\partial}{\partial t} + \tau_T \frac{\partial^2}{\partial t^2} \right) \nabla^2 \Phi = 0, \quad (29)$$

where  $\gamma = \alpha_T(3\lambda + 2\mu)$ ;  $\eta = \gamma T_0 / \lambda_0$ , and  $\mathbf{u} = \operatorname{grad} \Phi$ , with  $\Phi$  denoting the thermoelastic potential. It follows from (28) that

$$\nabla^2 \Phi - mT = g(t), \quad (30)$$

where  $g(t)$  is an indeterminate function of time;  $m = \gamma / (\lambda + 2\mu)$  and  $g(0) = 0$ ,  $g'(0) = 0$ .

We thus arrive at the following system of equations:

$$\begin{aligned} \nabla^2 \Phi - mT &= g(t), \\ \nabla^2 T - \frac{1}{a} \frac{\partial T}{\partial t} - \frac{1}{v_T^2} \frac{\partial^2 T}{\partial t^2} - \eta \left( \frac{\partial}{\partial t} + \tau_T \frac{\partial^2}{\partial t^2} \right) \nabla^2 \Phi &= 0. \end{aligned} \quad (31)$$

If we stipulate transient boundary conditions

$$\frac{\partial T}{\partial n} = f(t), \quad \frac{\partial \Phi}{\partial n} = \varphi(t), \quad (32)$$

at the boundary  $S$  of some region, then system (31) can be reduced to two separate equations. Let us integrate (31) over the volume of a body and then apply Green's identity, so that the equation of heat conduction becomes

$$\nabla^2 T - \left( m\eta + \frac{1}{a} \right) \left( \frac{\partial}{\partial t} + \tau_T \frac{\partial^2}{\partial t^2} \right) T = \eta \left[ \exp(-v_T^2 t) \int_0^t F(t') \exp(v_T^2 t') dt' (a - 1) - \tau_T F(t) \right], \quad (33)$$

where

$$F(t) = VS \left[ (1 - m\eta) \left( \frac{\partial}{\partial t} + \tau_T \frac{\partial^2}{\partial t^2} \right) \varphi(t) - m a f(t) \right]. \quad (34)$$

In (34)  $V$  denotes the volume and  $S$  denotes the surface of a body. It is evident, according to Eq. (33), that we have obtained here an equation of heat conduction with a heat source whose intensity is a function of

time. We may now write the following equation for the thermoelastic potential:

$$\nabla^2\Phi = mT + \frac{1}{v_T^2} \left[ \int_0^t F(t') dt' - \exp(-v_T^2 t) \int_0^t F(t') \exp(v_T^2 t') dt' \right]. \quad (35)$$

Instead of system (31), we have obtained two separate equations (33) and (35). The coupledness of the quasistatic thermoelasticity problem results, under transient boundary conditions, in the replacement of coefficient  $1/a$  by the coefficient  $[(1/a) + m\eta]$  in the equation of heat conduction with a concurrent appearance of a heat source. This result confirms the necessity of considering thermoelasticity problems coupled even in the quasistatic formulation.

#### NOTATION

|               |                                      |
|---------------|--------------------------------------|
| $J_i$         | is a flux;                           |
| $L_{ik}$      | are the thermodynamic coefficients;  |
| $\sigma$      | is the rate of entropy increase;     |
| $t$           | is the time;                         |
| $v_T$         | is the velocity of heat propagation; |
| $T$           | is the temperature;                  |
| $\varepsilon$ | is the energy;                       |
| $\mathbf{v}$  | is the velocity of a particle;       |
| $Q$           | is the amount of heat;               |
| $\mathbf{u}$  | is the displacement vector;          |
| $\rho$        | is the density of the medium;        |
| $m\eta$       | is the coupling coefficient.         |

#### LITERATURE

1. A. V. Lykov, Transfer Phenomenon in Capillary-Pore
2. A. V. Lykov, *Inzh.-Fiz. Zh.*, 9, No. 3 (1965).
3. A. V. Lykov, Theory of Heat Conduction [in Russian]
4. L. D. Landau and E. M. Lifshits, Statistical Physics
5. deGroot and P. Mazur, Nonequilibrium Thermodynamics (1964).
6. P. F. Muchnik and I. B. Rubashov, Methods of Heat-Shkola, Moscow (1970).
7. R. Shechter, Variational Method in Engineering Calculus (1971).
8. D. Seiman, Electrons and Phonons [Russian translation]
9. A. D. Kovalenko, Fundamentals of Thermoelasticity