On the variational principle of nonequilibrium nonlinear statistical thermodynamics

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(Submitted 28 May 1979)
Pis'ma Zh. Eksp. Teor. Fiz. **30**, No. 1, 52–55 (5 July 1979)

A vigorous variational principle is established for nonlinear nonequilibrium thermodynamic systems which follows from the generalized fluctuation-dissipation relationships.[1,2] An universal structure of the kinetic potential is obtained, which contains complete statistical information about the system.

PACS numbers: 05.70.Ln

In this report we shall point out an important consequence of the universal nonlinear fluctuation-dissipation relationships (FDR) obtained earlier.[1,2] We shall show, namely, that FDR provide a means for a rigorous formulation of the variational principle for irreversible transfer processes in any nonlinear system. In addition to this, FDR lead to the general expressions for the nonlinear transfer coefficients in terms of fluctuation characteristics of a system. A clear statistical physical interpretation of the variational principle (VP) is thereby established. Thus, our earlier results[1,2] may be used to provide a single-valued solution to the problem of the existence and form of the VP of nonlinear nonequilibrium thermodynamics, which has been widely discussed in the literature (see, e.g., Refs. 3–5) but has never been solved.

The transfer processes near thermodynamic equilibrium are described by the linear equations

$$I_a = \gamma_{a\beta} x_\beta \equiv I_a(x) \tag{1}$$

 0021-3640/80/010046-04$00.60

of continuity between the generalized flows I_α and forces x_α (which represent either a dynamic perturbation or the "thermostat" reaction with respect to deviation of a subject subsystem from an equilibrium state). By virtue of the Onsager reciprocal relation

$$\gamma_{\alpha\beta} = \gamma_{\beta\alpha} \tag{2}$$

Eq. (1) may be obtained from VP—conditions for the function maximum (in tensor notation)

$$\Lambda(I, x) = Ix - \frac{1}{2}(I\gamma^{-1}I + x\gamma x) = Ix - H(I, x), \qquad \delta\Lambda(I, x) = 0, \tag{3}$$

with respect to independent variations of forces and (or) flows.

As was shown earlier,[2] transfer equations in the nonlinear case may always be expressed in the form of Eq. (1), where $\gamma_{\alpha\beta} = \gamma_{\alpha\beta}(x)$ depend on the forces, are expressed in terms of nonequilibrium nonstationary fluctuation correlators, and at $x = 0$ do not conform to the reciprocal relation. The latter condition prevents extending the formulation of Eq. (3) to nonlinear systems.

Formulation of the VP is, however, made possible by an alternate general representation of the transport equations[2]

$$I_\alpha(x) = \lambda_{\alpha\beta}(x)x_\beta + \frac{1}{2!}\lambda_{\alpha\beta\gamma}(x)x_\beta x_\gamma + \ldots = \sum_{n=2}^{\infty}\frac{1}{(n-1)!}\lambda_n(x)x^{n-1}$$

$$= \left\{\frac{\partial}{\partial z_\alpha}F(z;x)\right\}_{z=x} \equiv \left\{\frac{\partial}{\partial z_\alpha}\sum_{n=2}^{\infty}\frac{1}{n!}\lambda_n(x)z^n\right\}_{z=x}, \tag{4}$$

where the tensors $\lambda_{\alpha\ldots\gamma}(x)$ are expressed directly in terms of the cumulants of stationary flow fluctuations and, with respect to their statistical definition,[2] are fully symmetrical (we should underscore this important fact). Furthermore, they always satisfy an infinite set of FDR,[2] from which, as may be shown, the following properties of the generating function $F(z;x)$ ensue: (1) $F(z;x) \geqslant 0$; (2) $F(z;x)$ is convex in z; (3) $F(x;x) = \frac{1}{2}x_\alpha I_\alpha(x) = \frac{1}{2}\mathscr{P}(x)$, where $\mathscr{P}(x)$ is the value of entropy production. Therefore, Eq. (4) may be obtained from the VP contained in the requirement of a function maximum

$$A(I, z, x) = I(z - x) - F(z; x) + F(x; x); \qquad \delta_z A(I, z, x) = 0, \tag{5}$$

with respect to variations z_α near a point $z_\alpha = x_\alpha$ or, in other words, local variations. The physical interpretation of such a VP is fully understood within the framework of the statistical approach being discussed and, the theory of irreversible processes, which is based on exact FDR. According to Eq. (4), the dependence of flows on the forces consists of two factors: (1) flows at fixed (local) values $\lambda_n(x)$, i.e., at fixed fluctuation and kinetic thermostat parameters and (2) for a thermostatic modulation of macroscopic flows (as a result of a nonlinear relation between these and fluctuation flows). Specifically, the second factor leads to perturbation of the reciprocal relation (we should mention that in a nonlinear system λ_n necessarily depends on x, according to FDR, i.e., a case $\lambda_n = \text{const}$ is impossible). The function

$$2[F(z;\tilde{x}) - F(x;\tilde{x})]$$

may be considered as excess production of entropy for the virtual force variations not affecting the thermostat state. Equations (4) and (5) show that a state in which the flow I_α vanishes corresponds to a minimum of entropy production relative to the virtual variations of the conjugate force z_α.

In the case of a purely phenomenological approach[3] it was noted in certain nonlinear problems that the VP and the required transport equations may be obtained by keeping the force under the sign of the kinetic coefficient invariant in $\mathscr{P}(x)$. The resultant function, which replaced $\mathscr{P}(x)$ and contained twice as many arguments, was referred to as the local kinetic potential. The same name may apply to the function $F(z,x)$ which was rigorously determined [Eq. (4)]. Naturally, a phenomenological approach can neither avoid involving the general determination of the kinetic potential nor explain its universal structure. It is impossible to even say whether a potential with the required properties always exists.

It is, therefore, remarkable that the very fact that a kinetic potential exists for any system and its clear universal structure [see Eq. (4) and formulas in Ref. 2], important properties 1–3 (as also a number of others, ensuing from FDR), and the physical sense which is fully clarified in the statistical theory, are all a necessary general consequence of nonlinear FDR. We thus have a general and statistically rigorous rule for formulating the kinetic potential and the associated VP form.

We shall show that the somewhat unusual (due to the additional requirement for locality) form of VP [Eq. (5)] may be replaced by a conventional one. Actually, the requirement for the function extremum [Eq. (5)] with respect to independent variations z and x automatically leads to the condition $z = x$ and Eq. (4). The "spare variable" z may generally be eliminated from the formulation of VP and the latter be made symmetrical with respect to forces and flows. For this reason we shall express z in terms of I from the equations

$$I_\alpha = \frac{\partial}{\partial z_\alpha} F(z;x),$$

which in view of the condition of convexity 2 always have a single-valued solution. Let us now introduce the following functions

$$H(I,x) = Iz(I) - F(z(I);x) + F(x;\tilde{x});$$
$$\Lambda(I,x) = Ix - H(I,x) = -A(I,z(I),x). \qquad (6)$$

It becomes easy to verify that the shape of VP

$$\delta \Lambda (I, x) = 0 \tag{7}$$

with respect to independent variations of forces and (or) flows leads to the transfer equation [Eq. (4)]. The extremal value $H(I,x)$ equals the entropy production $\mathscr{P}(x)$. The VP in Eqs. (7) and (6) is formally similar to Eq. (3) and, in the special case of a linear system, reduces to Eq. (3). The very substantial difference is attributed to the fact that in the nonlinear theory the function $H(I,x)$ [having the sense of entropy production for the virtual values of forces and flows which are not subordinated to Eq. (4)] is defined by the kinetic potential $F(z;x)$ which contains far more information than $\mathscr{P}(x)$ or even Eq. (4) (actually, it contains the total information on the fluctuations in a system).

The variational principle, Eqs. (5)–(7), may prove to be useful in both general formulation of nonlinear nonequilibrium thermodynamics and in the synthesis of absolute systems models and specific approximate calculations.

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