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Optimality of nonequilibrium systems and problems of statistical thermodynamics

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Abstract

This paper reviews advantages which stem from using methods of optimal control theory and variational calculus in nonequilibrium thermodynamics of transport phenomena, focusing on selected problems of statistical thermodynamics rather than on typical phenomenological descriptions. Neglected are aspects of thermodynamic stability and oscillatory phenomena, as those frequently considered earlier. The main problems discussed here are: statistical aspects of nonequilibrium conservation laws, work-producing devices described by master equations, and development of living systems governed by a complexity criterion based on information-theoretic entropy. These problems are presented mainly from the viewpoint of the contribution of the author and some associated researchers, yet an attempt is made to give a comparison of our results with those following from main work of others. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The purpose of this paper which originated from a conference talk [1] is to discuss the help that can be obtained from statistical theories when describing nonequilibrium thermodynamic systems. To illustrate contemporary tendencies, several problems of nonequilibrium statistical thermodynamics are analyzed, especially those which show visible link with macroscopic effects. Physical aspects of Boltzmann equation and its link with entropy and time arrow are not discussed; the reader is referred to books on nonequilibrium statistical mechanics and a paper by Lebovitz [1]. Section 2 treats the statistical aspect of connection between various representations of thermodynamics of nonequilibrium fluids with heat flow, and points out the role of a relationship (resembling the Gouy–Stodola law) which links energy and entropy representations. Section 3 applies this law and some results of Grad's [2] moment approach to pass from the entropy representation to the energy and Lagrangian representations of thermodynamics. Section 4 uses resulting Lagrangians to obtain the energy–momentum tensor for the fluid with heat flow and formulate associated conservation laws. Section 5 deals with work producing or work-consuming systems which are governed by master equations, i.e. their finite rate of energy dissipation and thermodynamic limits are described statistically. Issues such as: efficiency decrease caused by dissipation, finite rate bounds, and finite time generalization of the classical available energy (exergy) are main results in the classical limit when thermodynamic intensities can be defined. Section 6 refers to a recent work of Szwast [3] and reviews evolution of living organisms treated as multistage systems by the information-theoretic entropy. Finally, Section 7 addresses an extremality principle for a potential as a driving factor in the evolution dynamics, the potential being the entropy or an entropy-like complexity function. Classical thermodynamic quantities do not appear in this approach, yet the statistical model is governed by an extremum principle which, as in thermodynamics, implies extremal properties for a potential. A basic assumption of this work is that a bridge can be laid to link purely thermodynamic approaches with those which must abandon thermodynamics and rely on methods of statistical physics and information theory.

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Nomenclature

α	multiplier, heat coefficient
Γ	complexity
ρ	density
ω	frequency constant
σ_s	entropy production
A	area
$\mathcal{A}$	action
C	peculiar velocity
c	specific heat
e	energy
G	fluid flowrate
g, g_1	conductances
H	Hamiltonian
$\mathbf{j}$	flux density
k	rate constant
L	kinetic potential
m	mass
n	stage number
p_i	probabilities
P	pressure
$\mathbf{Q}$	energy flux
$\mathbf{q}$	heat flux
R	gas constant
R_j	chemical resistance
r_j	rate of jth reaction
S	information entropy
S_σ	dissipated entropy
s	specific entropy
T	temperature
$\mathbf{u}$	macroscopic velocity
$\mathbf{v}$	diffusion velocity
V	potential
W	total work
w	specific work
$\mathbf{x}$	radius vector
z	adjoint variable

2. Nonequilibrium fluids with heat flow in various representations of thermodynamics

Here our task is to develop the thermodynamics of heat flow without local equilibrium. The description obtained will next be used to construct suitable Lagrangians, variational principles and conservation laws. We work in the framework of extended thermodynamics of fluids [5].

Consider a one-component fluid conducting heat at state A, Fig. 1, off but near the Gibbs surface (BDC) when the local equilibrium assumption is inapplicable. The energy of a fluid's element moving with the moving frame of reference is the nonequilibrium internal energy. This internal energy depends not only on the usual state variables (wherever they have meaning), but also on nonequilibrium variables such as heat flux or diffusive entropy flux. Here we select the diffusive entropy flux, $\mathbf{j}_s$, as the nonequilibrium variable of choice. It is treated as an unconstrained internal variable which relaxes to equilibrium.

The nonequilibrium energy density ρ_e of the fluid (or its specific energy e) is a function of the fluid density ρ, specific entropy s and diffusive entropy flux $\mathbf{j}_s$, the relaxing variable. The equilibrium internal energy density ρe^{eq} of a stable system is the minimum of ρe with respect to unconstrained relaxing $\mathbf{j}_s$ at constant ρ and s. As $\rho = v^{-1}$, the specific volume, the minimum of ρe (or e itself) with respect to $\mathbf{j}_s$, occurs at constant specific entropy s and volume v which are the proper variables at which the energy attains extremum at equilibrium. This is, of course, well known from classical thermodynamics [6]. Since $\mathbf{j}_s$ is a diffusive flux, the minimum occurs at $\mathbf{j}_s = 0$.

In the absence of an external magnetic field the rotation of the system does not change the form of the nonequilibrium function $e(s, \rho, \mathbf{j}_s)$ which depends then only on the length of the vector $\mathbf{j}_s$; compare the kinetic

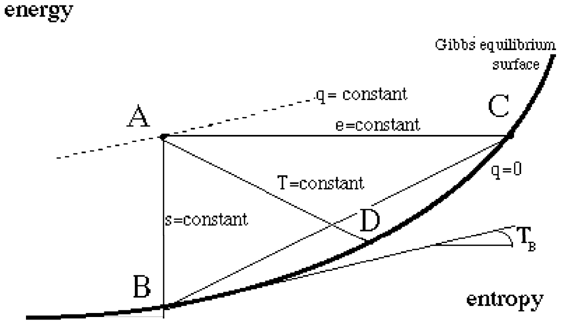

Fig. 1. Arbitrariness of the equilibrium reference state chosen for given nonequilibrium state, point A. Three various equilibrium states at the points B and C and D correspond to the energy, entropy and free energy representation, respectively. An observer, knowing ρ and e (from an experiment or a computation) formulates his description of the state A in terms of the equilibrium parameters at C for the arbitrary set of nonequilibrium variables (here the heat flux $\mathbf{q}$ or the entropy flux $\mathbf{j}_s$). However, one who knows ρ and s (e. g., from distribution function f corresponding to A) can base his equations on the equilibrium properties at B. When point A moves the background equilibrium states (B, C and D) vary in time. The conventional picture of motion in terms of Hamilton's principle corresponds to following the behavior of B and the kinetic energy of entropy flux, whereas the kinetic theory view corresponds to tracking of C and the deviation of entropy from equilibrium. The transition from one view to the other is possible [4].

theory expression, e.g., Eq. (24). The following is the McLaurin expansion of e with respect to $\mathbf{j}_s$ in the vicinity of equilibrium ($\mathbf{j}_s = 0$);

$$e(s,\rho,\mathbf{j}_s) = e(s,\rho,0) + \frac{1}{2}\left(\partial^2 e/\partial \mathbf{j}_s^2\right)_{s,\rho}\mathbf{j}_s^2 + 0(s,\rho,\mathbf{j}_s), \tag{1}$$

where $e(s,\rho,0) = e(s,\rho)$ is the equilibrium function of specific energy well known in thermostatics. Since $(\partial e/\partial j_s)_{\rho,s} = 0$ at equilibrium, the first-order term disappears from expansion (7), and the first nonvanishing nonequilibrium term is the term quadratic with respect to $\mathbf{j}_s$. This notion pertains, of course, to any variable which vanishes at equilibrium. It has to be remembered that the second derivative $(\partial^2 e/\partial \mathbf{j}_s^2)$ in Eq. (1) is determined at constant s and ρ and hence it depends on these quantities as parameters. The same constraints apply also to the third- and higher-order terms.

Consequently with $\mathbf{j}_s$ as the only independent variable pertaining to nonequilibrium behavior, and not to far from equilibrium (i.e., not in the basin of a limit cycle, for example), the specific internal energy of a nonequilibrium state can be expressed as:

$$e(s,\rho,\mathbf{j}_s) = e(s,\rho,0) + \Delta e(s,\rho,\mathbf{j}_s), \tag{2}$$

where

$$\Delta e = \frac{1}{2}(\partial^2 e/\partial \mathbf{j}_s^2)_{s,\rho}\mathbf{j}_s^2 + 0(s,\rho,\mathbf{j}_s) \tag{3}$$

is the nonequilibrium correction to the internal energy; for sufficiently small $\mathbf{j}_s$, Δe can always be approximated by its $\mathbf{j}_s^2$ term.

From Eq. (2) the following general equation for the perfect differential of the specific internal energy e is deduced:

$$\begin{aligned} \mathrm{d}e(s,\rho,\mathbf{j}_s) &= \mathrm{d}(e^{\mathrm{eq}} + \Delta e) \\ &= (\partial e^{\mathrm{eq}}/\partial s + \partial \Delta e/\partial s)\mathrm{d}s + (\partial e^{\mathrm{eq}}/\partial \rho \\ &\quad + \partial \Delta e/\partial \rho)\mathrm{d}\rho + \partial \Delta e/\partial \mathbf{j}_s.\mathrm{d}\mathbf{j}_s \\ &= [T(s,\rho) + \Delta T(s,\rho,\mathbf{j}_s)]\mathrm{d}s + \rho^{-2}[P(s,\rho) \\ &\quad + \Delta P(s,\rho,\mathbf{j}_s)]\mathrm{d}\rho + \mathbf{a}_s(s,\rho,\mathbf{j}_s)\cdot \mathrm{d}\mathbf{j}_s. \end{aligned} \tag{4}$$

Eq. (4) defines the corrections ΔT and $\Delta \rho$ which should be added to $T(\rho,\mathrm{s})$ and $P(\rho,s)$ to obtain the proper values of the derivatives $\partial e/\partial s$ and $\partial e/\partial \rho$, Eqs. (7) and (8). In the so-called energy representation of thermodynamics [6,7], the space spanned by s and ρ takes on $\mathbf{j}_s$ as an extra variable. For a given nonequilibrium state A, the equilibrium state corresponds in this representation to the point B in Fig. 1. Other reference equilibrium states can be used depending on the basic thermodynamic variables used; see, e.g., points C and D in Fig. 1 for isoenergetic ($e =$ constant) and isothermal equilibrium. They correspond, respectively, with using the entropy and free energy as potentials, i.e., with the entropy and free energy representations. Where the choice of definition is important and not explicit, the subscript notation will be used to distinguish the reference equilibrium quantities; i.e., symbols $T_{(\mathrm{B})}, P_{(\mathrm{C})}$, etc., will be used or the variables of definite representations will be specified. From Eq. (4) one obtains the quantities

$$T(s,\rho,\mathbf{j}_s) = T(s,\rho) + \Delta T(s,\rho,\mathbf{j}_s), \tag{5}$$

$$P(s,\rho,\mathbf{j}_s) = P(s,\rho) + \Delta T(s,\rho,\mathbf{j}_s). \tag{6}$$

These are customarily called “nonequilibrium temperatures and pressures”. However, they are limited in the sense that *they are only measures of partial derivatives of the energy with particular variables* chosen to be held constant in the particular frame of variables which includes ρ and s, namely:

$$T(s,\rho,\mathbf{j}_s) = \partial e(s,\rho,\mathbf{j}_s)_{\rho,j_s}/\partial s \tag{7}$$

$$P(s,\rho,\mathbf{j}_s) = \rho^2 \partial e(s,\rho,\mathbf{j}_s)_{\rho,j_s}/\partial \rho. \tag{8}$$

The last quantity we define is the vector variable $\mathbf{a}_s(s,\rho,j_s)$ adjoint with respect to the entropy flux $\mathbf{j}_s$ such that

$$\mathbf{a}_s(s,\rho,\mathbf{j}_s) = \partial \Delta e(s,\rho,\mathbf{j}_s)_{\rho,s}/\partial \mathbf{j}_s. \tag{9}$$

We will also use the entropy flux adjoint based on the correction to the energy of unit volume $\Delta(\rho e)$

$$\mathbf{i}_s(s,\rho,\mathbf{j}_s) = \partial \Delta \rho e(s,\rho,\mathbf{j}_s)_{\rho,s}/\partial \mathbf{j}_s \tag{10}$$

which has the dimension of momentum per unit entropy and is more important than $\mathbf{a}_s$. The significance of $\mathbf{a}_s$ and $\mathbf{i}_s$ will be shown later (Section 3). Restricted to the quadratic approximation of Δe in Eq. (1) in the case of small flux $\mathbf{j}_s$, on the basis of Eqs. (2), (3), (7) and (8) the “nonequilibrium corrections” ΔT and ΔP caused by the presence of flux $\mathbf{j}_s$ are

$$\Delta T(s,\rho,\mathbf{j}_s) = \frac{1}{2}(\partial^3 \Delta e/\partial \mathbf{j}_s^2 \partial s)^{\mathrm{eq}}\mathbf{j}_s^2, \tag{11}$$

$$\Delta P(s,\rho,\mathbf{j}_s) = \frac{1}{2}\rho^2(\partial^3 \Delta e/\partial \mathbf{j}_s^2 \partial \rho)^{\mathrm{eq}}\mathbf{j}_s^2, \tag{12}$$

i.e., they are quadratic functions of $\mathbf{j}_s$. From Eqs. (3) and (10) the entropy flux adjoint $\mathbf{i}_s$ is

$$\mathbf{i}_s = \left(\partial^2 \rho e(s,\rho,\mathbf{j}_s)/\partial \mathbf{j}_s^2\right)\mathbf{j}_s. \tag{13}$$

In Eqs. (11)–(13) the equilibrium superscript means that the corresponding derivatives are evaluated at $\mathbf{j}_s = 0$. Therefore the coefficients of $\mathbf{j}_s$ in Eqs. (11)–(13) depend on the classical variables (s,ρ) exclusively, so long as the expansion (1) around equilibrium is applicable. The reason we consider the energy representation is that it is the most natural representation for the extension of Hamilton’s principle which we are going to investigate. If however the thermodynamic space is spanned by the variables e, ρ and $\mathbf{q}$ one naturally uses the entropy representation [6].

By considering the expansion of the entropy around the isoenergetic equilibrium with respect to unconstrained flux $\mathbf{q}$ (or $\mathbf{j}_s$) one can obtain the formalism analogous to that presented here in energy representation. The corresponding formulae are omitted. It is important to realize that *for a single nonequilibrium state of the system the use of the entropy representation and energy representation establish two different equilibrium states located on the Gibbs surface, Fig. 1*. This of course, is because of the difference in what is held constant. The distance between these two equilibrium states (B and C, Fig. 1) understood e.g. as the Weinhold distance [7,8] or equivalent probability distance [9] increases with the distance of the state A from the Gibbs surface. This distance can also be measured in terms of the modulus of the flux $\mathbf{j}_s$ or in terms of the module of the excesses $\Delta e = \mathrm{AB}$ or $\Delta s = \mathrm{AC}$. When the curvature of the Gibb's surface can be neglected, corresponding to the near-equilibrium situation, the two excesses are linked by an equality resembling the Gouy–Stodola law [6,10]).

$$\Delta e = -T\Delta s. \tag{14}$$

Both equilibrium temperatures pertaining to the points B or C or nonequilibrium temperature T at A are acceptable in Eq. (14) in the near equilibrium case. In this case, any conventional variable ($P, T \ldots$ etc.) can be replaced by its equilibrium values ($P^{\mathrm{eq}}, T^{\mathrm{eq}} \ldots$etc.) in the *multiplicative coefficients* of any relationship.

3. From entropy to energy corrections by using kinetic theory

It is essential to recognize that the entropy representation is natural for the formalism of the kinetic theory [2] in which, by definition, the internal energy comprises the only contribution except that of macroscopic motion $\mathbf{u}^2/2$ and external field. Hence the specific energy of an ideal gas or fluid with heat is equal to the specific energy at equilibrium C in Fig. 1. The only temperatures and pressures that appear in the expressions of kinetic theory are $T_{(\mathrm{C})}$ and $P_{(\mathrm{C})}$. From this formalism one determines the nonequilibrium corrections Δs or Δe in terms of the nonequilibrium density distribution function f. Here, for the reader's convenience, we recapitulate the results of several works ([2,4], and others) for dilute gas of rigid spheres in the relaxation time approximation of the Boltzmann equation. The molecular velocity distribution function f, out of equilibrium but close to it, is given in the form

$$f(\mathbf{C}) = f^{\mathrm{eq}}(\mathbf{C})(1+\phi_1), \tag{15}$$

where f is the local equilibrium (Maxwell–Boltzmann) distribution pertaining to the entropy representation equilibrium (point C, Fig. 1). f and f^{eq} are scalars, but functions of the peculiar velocity $\mathbf{C} = \mathbf{c}$ - $\mathbf{u}$, and ϕ_1 is a function of the deviation from equilibrium. This deviation is expressed in terms of the ∇T in the Chapman–Enskog method and in terms of the heat flux $\mathbf{q}$ in Grad's method.

Using Eq. (15) in the definition of entropy, one integrates the expression $f \ln f$ over all of the space of the molecular velocity $\mathbf{c}$,

$$\rho s = -k_{\mathrm{B}} \int f \ln f \, \mathrm{d}\mathbf{c}. \tag{16}$$

Proceeding with development of s up to second-order in ϕ_1, one obtains

$$\rho s = (\rho s)^{\mathrm{eq}} + (\rho s)^{(1)} + (\rho s)^{(2)}, \tag{17}$$

with local equilibrium entropy

$$(\rho s)^{\mathrm{eq}} = -k_{\mathrm{B}} \int f^{\mathrm{eq}} \ln f^{\mathrm{eq}} \, \mathrm{d}\mathbf{c} \tag{18}$$

and nonequilibrium correction

$$(\rho s)^{(1)} = -k_{\mathrm{B}} \int f^{\mathrm{eq}} \phi_1 \ln f^{\mathrm{eq}} \, \mathrm{d}\mathbf{c} = 0. \tag{19a}$$

This proves again that one deals with the entropy representation where the entropy is maximum at equilibrium. In the energy representation the analogous equation is

$$(\rho e)^{(1)} = \int f^{\mathrm{eq}} \phi_1 m \mathbf{c}^2 \, \mathrm{d}\mathbf{c} = 0, \tag{19b}$$

which corresponds to reaching the minimum energy. The second-order correction to the entropy density (in entropy representation) is

$$(\rho s)^{(2)} = \rho \Delta s = -\frac{1}{2} k_{\mathrm{B}} \int f^{\mathrm{eq}} \phi_1^2 \, \mathrm{d}\mathbf{c}. \tag{20}$$

Hence, in view of the relation between Δe and Δs implied by Fig. 1 or Eq. (14)

$$\Delta \mathrm{e} = -k_{\mathrm{B}} T/(2\rho) \int f^{\mathrm{eq}} \phi_1^2 \, \mathrm{d}\mathbf{c}. \tag{21}$$

Since the state is close to the equilibrium surface, the multiplicative factors containing conventional thermodynamic variables can always be evaluated at arbitrary equilibrium points (B, C, or D in Fig. 1). However in the formulas such as Eqs. (15), (22) and (23) they were evaluated (in the kinetic theory) for the case of the isoenergetic equilibrium (point C, Fig. 1). The function ϕ_1, obtained in Grad's method when the system's disequilibrium is maintained by a (vector) heat flux $\mathbf{q}$ is

$$\phi_1 = \frac{2}{5}(m/Pk_{\mathrm{B}}^2 T^2)\left[\frac{mC^2}{2} - \frac{5}{2}kT\right]\mathbf{C}\cdot\mathbf{q}, \tag{22}$$

where m is the mass of a molecule [2,5]. From Eqs. (20)–(22) one obtains for the entropy deviation

$$\Delta s = -(m/5\rho P k_{\mathrm{B}} T^2)\mathbf{q}^2 \tag{23}$$

and for the energy deviation, Eq. (14), in terms of the entropy flux $\mathbf{j}_\mathrm{s} = \mathbf{q}T^{-1}$

$$\Delta e = (1/5)(m^2/k_\mathrm{B}^2\rho^2)\mathbf{j}_\mathrm{s}^2 = \rho^{-2}g\mathbf{j}_\mathrm{s}^2/2. \tag{24}$$

Eqs. (23) and (24) hold to the accuracy of the thirteenth moment of the velocity [2]. When passing from Eqs. (23) and (24) the state equation $P = \rho k_\mathrm{B}Tm^{-1}$ was used and the constant g is defined as

$$g = \frac{2mT\rho}{5PK_\mathrm{B}} = \frac{2m^2}{5k_\mathrm{B}^2}. \tag{25}$$

In this way we abandoned the entropy representation. The pressure in Eqs. (22) and (25) is the ideal gas pressure, given by the definition used in the kinetic theory [2]. Eq. (24) with constant g defined by Eq. (25) is the characteristic feature of the ideal monoatomic gas (dilute Boltzmann gas composed of hard spheres). For arbitrary fluids (polyatomic gases, dense monoatomic gases and liquids) one can retain the form of the last expression in Eq. (24) by using a general definition of g obtained by comparing Eqs. (2) and (24),

$$g(\rho, s) = (\rho^\mathrm{eq})^2(\partial^2 e/\partial\mathbf{j}_\mathrm{s}^2)^\mathrm{eq}. \tag{26}$$

In the ideal gas case the derivative $\partial^2 e/\partial\mathbf{j}_\mathrm{s}^2 = (2/5)(m^2/k^2\rho^2)$ from Eq. (24) and the definition (25) is immediately recovered given the definition (26). Eq. (26) applies a hypothesis about the equality of the kinetic and static nonequilibrium energy corrections in a thermal shock wave front Sieniutycz's [11]. The hypothesis can be used to compute $(\partial^2 e/\partial\mathbf{j}_\mathrm{s}^2)^\mathrm{eq}$ for arbitrary fluids as $T/(\rho c_\mathrm{p}G)$ and hence g as $T\rho/(c_\mathrm{p}G)$, where G is the shear modulus. Equilibrium values of thermodynamic parameters can be applied in such expressions. For the ideal gas the shear modulus is just the pressure P (a result known by Maxwell) and $c_\mathrm{p} = 5k/(2m)$. These result allow one to recover definition (25) from the expression $g = T\rho/(c_\mathrm{p}G)$; they support the hypothesis mentioned above. However, for the purpose of general considerations the use of the implicit dependence of g on the basic variables (ρ, s) will be enough, i.e., the function $g(\rho, s)$ will be used when passing to arbitrary fluids. Eq. (24) shows that when the coordinates s, ρ (or v) and $\mathbf{j}_\mathrm{s}$ are used then (with accuracy to second-order terms) the nonequilibrium energy correction of an ideal gas does not depend explicitly on entropy s. In the energy representation, the "nonequilibrium corrections" ΔT and ΔP obtained from Eqs. (5)–(8) are, respectively,

$$\Delta T(s, \rho, \mathbf{j}_\mathrm{s}) = 0 \tag{27}$$

and

$$\Delta P(s, \rho, \mathbf{j}_\mathrm{s}) = \rho^2(\partial\Delta e/\partial\rho)_{s,\mathbf{j}_\mathrm{s}} = -g\rho^{-1}\mathbf{j}_\mathrm{s}^2. \tag{28}$$

The entropy flux adjoints $\mathbf{a}_\mathrm{s}$ and $\mathbf{j}_\mathrm{s}$, Eqs. (9) and (10), are, respectively,

$$\mathbf{a}_\mathrm{s} = (\partial\Delta e/\partial\mathbf{j}_\mathrm{s})_{s,\rho} = g\rho^{-2}\mathbf{j}_\mathrm{s}. \tag{29a}$$

and

$$\mathbf{i}_\mathrm{s} = g\rho^{-2}\mathbf{j}_\mathrm{s} = gs\mathbf{v}_\mathrm{s} = gs(\mathbf{u}_\mathrm{s} - \mathbf{u}). \tag{29b}$$

The entropy diffusion velocity $\mathbf{v}_\mathrm{s} = \mathbf{u}_\mathrm{s} - \mathbf{u} = \mathbf{j}_\mathrm{s}/\rho s = \mathbf{j}_\mathrm{s}/\rho_\mathrm{s}$ was introduced in Eq. (29b). One could also introduce there the product $k_\mathrm{B}gs$ which has the dimension of mass. For the ideal gas this product is $m_\mathrm{s} = 2/5(m^2sk_\mathrm{B}^{-1})$ which is a measure of heat inertia. Eqs. (27)–(29b) can also be obtained from Eqs. (11)–(13).

From Eqs. (27) and (28) one has for an ideal gas in energy representation

$$T(s, \rho, \mathbf{j}_\mathrm{s}) = T(s, \rho, 0) \equiv T(s, \rho)^\mathrm{eq} \tag{30}$$

and

$$\begin{aligned} P(s, \rho, \mathbf{j}_\mathrm{s}) &= P(s, \rho, 0) - g\rho^{-1}\mathbf{j}_\mathrm{s}^2 \\ &\equiv P(s, \rho)^\mathrm{eq} - g\rho^{-1}\mathbf{j}_\mathrm{s}^2. \end{aligned} \tag{31}$$

These formulae link the intensities T and P at the points A and B in Fig. 1. Note that $e \neq e^\mathrm{eq}$ in this representation (Fig. 1, points A and B).

The nonequilibrium temperatures and pressures were considered by Jou and Casas-Vazquez [12] in the entropy representation. An experiment has also been suggested to directly check their physical reality based on assumption that a thermometer reads the nonequilibrium rather than local equilibrium T. They defined nonequilibrium corrections to equilibrium quantities in terms of the partial derivatives of the function $s(e, \rho^{-1}, \mathbf{q})$ with respect to e and ρ^{-1} taken at constant $\mathbf{q}$ rather than constant $\mathbf{j}_\mathrm{s}$. Here, however, "nonequilibrium" T and P are defined in terms of the partial derivatives of the nonequilibrium energy $e(s, \rho^{-1}, \mathbf{j}_\mathrm{s})$ with respect to s and ρ (or $\rho^{-1} = v$) taken at constant $\mathbf{j}_\mathrm{s}$. In fact, in order to preserve the invariance of dissipation the entropy flux should be taken as the proper variable of the energy representation [13]; thus the change of the variable from $\mathbf{q}$ to $\mathbf{j}_\mathrm{s}$ is madatory. Furthermore, the reference (equilibrium) states are not equivalent in the two representations. When this distinction is kept in mind the results become consistent. As Eq. (30) indicates T contained therein is equal to the equilibrium temperature $T(\rho, s)$ which is both the measure of mean kinetic energy of an equilibrium and the derivative of energy with respect to the entropy. This equality occurs because we chose the entropy flux $\mathbf{j}_\mathrm{s}$, not the heat flux $\mathbf{q}$, as the nonequilibrium variable in energy function e. If one differentiates the nonequilibrium entropy s with respect to the energy holding $\mathbf{q}$ constant, then one obtains the reciprocal of the nonequilibrium temperature of Jou and Casas-Vazques [12] $T_{(\mathrm{C})}$ which differs from the reciprocal of the corresponding equilibrium temperature T^eq by a term quadratic in $\mathbf{q}$. In general the "nonequilibrium temperatures" (understood as the fifth moment of the both nonequilibrium and equilibrium density functions) are not the measures of mean kinetic energy. It is known that in the kinetic theory

$$\frac{3}{2}k_{\mathrm{B}}T_{(\mathrm{C})}n = \int \frac{1}{2}m\mathbf{C}^2 f\,\mathrm{d}\mathbf{c} = \int m\mathbf{C}^2 f^{\mathrm{eq}}\,\mathrm{d}c, \tag{32}$$

so that $f\phi_1$ does not contribute to the fifth (first four) moments of the nonequilibrium distribution function [2,12,14]). Here $T_{(\mathrm{C})}$ is derivative $(\partial s/\partial e)^{-1}_{\mathbf{j}_{\mathrm{s}}=0}$ pertaining to isoenergetic equilibrium at $e=\text{constant}$. The nonequilibrium intensities discussed here should be understood as no less and no more than definitive partial derivatives of the nonequilibrium energy [or measures of these derivatives as, e.g. in Eq. (4)] computed for definite variables. The same pertains to the corrections ΔT and ΔP. They are generated here for the purpose of concrete calculations but the question of the proper (natural) set of nonequilibrium variables in e still needs more investigation. In what follows we describe the nonequilibrium states in terms of the equilibrium quantities of definite representation and nonequilibrium fluxes ($\mathbf{j}_{\mathrm{s}}$ or $\mathbf{q}$). Such a description is representation dependent and thus needs careful handling; however, it allows one to exploit the standard transformations of classical equilibrium thermodynamics. Similar problems arise for the chemical potential. The consequences of the nonequilibrium contributions to the chemical potential has been studied in polymers and in suspensions [5]. An extension of the classical Einstein's formula linking mobility and diffusion coefficients shows that the drift contribution to μ equals $-mu^2/2$, then higher terms appear.

The nonequilibrium temperatures T, pressures P and chemical potentials μ are considered here under the assumption that the specification of the extended state (classical static variables and flux densities) is sufficient to define the thermodynamics of the system in question. The statistical aspects of nonequilibrium thermodynamic intensities were investigated by Keizer in his theory of elementary molecular processes that drive the system deterministically and determine the extent of fluctuations. This leads to a generalization of the entropy hessian based on the theory of nonequilibrium fluctuations [15, see also Section 5]). The theory of steady states leads to a transition probability formula with covariance matrix differing from that at equilibrium. Due to this difference, the thermodynamic intensities, the formal derivatives in the Gibbs formula, differ from their equilibrium values.

4. Nonequilibrium Gibbs equations, Lagrangians and conservation laws

The results discussed above help obtain two basic quantities which characterize the moving nonequilibrium gas, the total energy density, E, and the corresponding kinetic potential L, and to give explicit formulae for perfect derivatives of these quantities. The formulae will be next exploited in Chap. 5 to accomplish the important goal: to determine components of the energy–momentum tensor and corresponding conservation laws for the fluid with heat flow.

In the energy representation, the total volumetric energy E of a nonequilibrium fluid which moves with the hydrodynamic velocity $\mathbf{u}$ [mass flux $\mathbf{J}=\rho\mathbf{u}$] is described by a formula

$$E(\rho, s, \mathbf{j}_{\mathrm{s}}, \mathbf{J}) = \rho e^{\mathrm{eq}}(s,\rho) + \frac{1}{2}\rho^{-1}g\mathbf{j}_{\mathrm{s}}^2 + \frac{1}{2}\rho^{-1}\mathbf{J}^2 + \rho\psi(\mathbf{x},t), \tag{33}$$

where $\psi(\mathbf{x},t)$ is the external gravitational field. The first two terms on the right hand side, respectively, describe densities of the internal energy at equilibrium and the nonequilibrium component of internal energy. The last two terms, respectively, express densities of kinetic and potential energy. In the entropy representation total energy (33) becomes (Fig. 1)

$$E(\rho, e, \mathbf{q}, \mathbf{J}) = \rho e + \frac{1}{2}\rho^{-1}\mathbf{J}^2 + \rho\psi(\mathbf{x},t) \tag{34}$$

which is just the usual energy formula used in the nonequilibrium thermodynamics and kinetic theory. Note that in this representation the energy E does not contain explicitly the nonequilibrium variable, which is in this case the heat flux, $\mathbf{q}$. However, this flux appears in the nonequilibrium correction to the entropy function, Eq. (23). The related equilibrium energy density is simply $\rho_{e^{\mathrm{eq}}} = \rho e$. Comparison of two representations reveals an effect of appearance or disappearance of various "kinetic" terms when passing from one to another representation. This is caused by the difference between the equilibrium reference states (B and C). Further, to state the Hamilton's principle, the energy representation is used.

Below we write down the perfect differentials of energy (Gibbs equations) for the case of the ideal hard sphere gas where g is the constant given by Eq. (25). The perfect differential of E, Eq. (33), has the form

$$\mathrm{d}E = \rho T^{\mathrm{eq}}\mathrm{d}s + \left(P^{\mathrm{eq}}\rho^{-1} + e^{\mathrm{eq}} - \frac{1}{2}g\rho^{-2}\mathbf{j}_{\mathrm{s}}^2 - \frac{1}{2}\mathbf{u}^2 + \psi\right)\mathrm{d}\rho + g\rho^{-1}\mathbf{j}_{\mathrm{s}}.\mathrm{d}\mathbf{j}_{\mathrm{s}} + \mathbf{u}.\mathrm{d}\mathbf{J} - \rho\mathbf{F}.\mathrm{d}\mathbf{x} + \rho\psi_{\mathrm{t}}\mathrm{d}t \tag{35}$$

where $\mathbf{u}=\mathbf{J}/\rho$, $\mathbf{F}=-\nabla\psi$ (the external force), $\psi_{\mathrm{t}}=\partial\psi/\partial t$, and the equilibrium reference temperature $T^{\mathrm{eq}}=(\partial e^{\mathrm{eq}}/\partial s)_\rho$. In Eq. (35) variables typical of the Eulerian fluid theory (with the extra variable $\mathbf{j}_{\mathrm{s}}$) are used to express the total differential of the volumetric energy. When more popular variables $\rho s, \rho, \mathbf{u}=\mathbf{J}/\rho$ are used and the velocity of the entropy diffusion $\mathbf{v}_{\mathrm{s}}=\mathbf{j}_{\mathrm{s}}/(\rho s)$ is introduced then Eq. (35) takes a more familiar form (36),

$$\mathrm{d}E = (T^{\mathrm{eq}} + gs\mathbf{v}_{\mathrm{s}}^2)\mathrm{d}(\rho s) + (\mu^{\mathrm{eq}} + \psi + u^2/2 + g\rho v_{\mathrm{s}}^2)\mathrm{d}\rho + gs\mathbf{j}_{\mathrm{s}}\cdot\mathrm{d}\mathbf{v}_{\mathrm{s}} + \mathbf{J}\cdot\mathrm{d}\mathbf{u} - \rho\mathbf{F}\cdot\mathrm{d}\mathbf{x} + \rho\psi_{\mathrm{t}}\mathrm{d}t, \tag{36}$$

where $\mu^{\mathrm{eq}} = (\partial \rho e^{\mathrm{eq}}/\partial \rho)_{\rho s}$ is the equilibrium chemical potential. Finally we find the perfect differential of the specific total energy $e = E/\rho$, a counterpart of Eq. (4),

$$\begin{aligned}\mathrm{d}(E/\rho) = T^{\mathrm{eq}}\mathrm{d}s + (P^{\mathrm{eq}} - gv\mathbf{j}_{\mathrm{s}}^2)\mathrm{d}v + vgs\mathbf{v}_{\mathrm{s}}\mathbf{j}_{\mathrm{s}} \cdot \mathrm{d}\mathbf{j}_{\mathrm{s}} \\ + \mathbf{u} \cdot \mathrm{d}\mathbf{u} - \mathbf{F} \cdot \mathrm{d}\mathbf{x} + \psi_t \mathrm{d}t,\end{aligned} \tag{37}$$

which is consistent with derivatives described by Eqs. (29a)–(31). We purposely have given here the several equivalent energy Eqs. (34)–(36) because it is instructive to observe how various derivatives ($\partial E/\partial s$, $\partial e/\partial s$, etc.) depend on the irreversible flux $\mathbf{j}_{\mathrm{s}}$ in the system. The specific results obtained above incorporate the assumption of constancy of coefficient g, Eq. (25), which is the property of the ideal gas. The nonequilibrium corrections to classical thermodynamic quantities depend crucially on the variability of g with conventional state variables and reference equilibrium state. Therefore Eqs. (35)–(37) may be of limited use for fluids which do not obey Clapeyron's equation (e.g. liquids). In those cases the use of variable $g = T\rho/(c_{\mathrm{p}}G)$ based on shear modulus G, as discussed above, is recommended. Alternatively, one can rely on other specific models of thermal inertia.

We shall now tend to derive conservation laws from an optimality principle for the physical action. As the process variables we use isoentropic equilibrium temperature $T^{\mathrm{eq}}(\rho, s)$ and pressure $P^{\mathrm{eq}}(\rho, s)$ and nonequilibrium corrections (for definite variables) as functions of $\mathbf{v}_{\mathrm{s}}^2$ or $\mathbf{j}_{\mathrm{s}}^2$. The fundamental quantity from the viewpoint of variational analysis is the kinetic potential **L**. We will see that, from the viewpoint of thermodynamics, **L** is not less valuable thermodynamic potential than those more popular others. Any use of **L** as thermodynamic potential is allowed, provided that the standard thermodynamic requirement is met: **L** is expressed in terms of its natural variables in the sense of Callen [6].

In Eulerian fluid mechanics the classical kinetic potential L^0 is the Legendre transformation of the energy density with respect to the density of momentum ($\rho\mathbf{u}$ or $\mathbf{J}$, in the nonrelativistic case). This result comes, of course, from the mechanics of material points. However, in the case of a nonequilibrium fluid described by Eq. (34) the situation is more involved because the energy may change not only by the motion of mass (the **J** flux) but also by the motion of entropy (the $\mathbf{j}_{\mathrm{s}}$ flux). Consequently one has to decide whether to use the conventional Legendre transform with **J** only, or to choose an extended (double) Legendre transform, using both **J** and $\mathbf{j}_{\mathrm{s}}$ or **J** and $\mathbf{i}_{\mathrm{s}}$. Our tests in a previous work [4] show that only the extended kinetic potential, Eq. (38), allows one to recover the proper energy formula, Eq. (33), from the approach through Hamilton's principle. In other words, only the extended (double) Legendre transform is correct

$$\mathbf{L} = \mathbf{J}.\partial E/\partial \mathbf{J} + \mathbf{j}_{\mathrm{s}}.\partial E/\partial \mathbf{j}_{\mathrm{s}} - E(\rho, s, \mathbf{J}, \mathbf{j}_{\mathrm{s}}). \tag{38}$$

Due to the linearity of relationship linking $\mathbf{j}_{\mathrm{s}}$, $\mathbf{a}_{\mathrm{s}}$, and $\mathbf{i}_{\mathrm{s}}$ the use of $\mathbf{a}_{\mathrm{s}}$ or $\mathbf{i}_{\mathrm{s}}$ in Eq. (38) is still correct. The use of the entropy flux in Eq. (38) in the framework of linear theory is the matter of convenience. In fact, the arbitrariness of use $\mathbf{j}_{\mathrm{s}}$, $\mathbf{a}_{\mathrm{s}}$, or $\mathbf{i}_{\mathrm{s}}$ holds only in the case when each of these quantities is proportional to the momentum density $\mathbf{i}_{\mathrm{s}}$ associated with the density of entropy flux $\mathbf{j}_{\mathrm{s}}$. This variable is called the thermal momentum, and it is the proper or natural variable in E when the energy is transformed into the Lagrangian. We have shown benefits resulting from the use of the thermal momentum in many circumstances. Eq. (38) is correct because works with variables proportional to respective momentum densities.

To obtain the energy–momentum tensor and corresponding conservation laws we shall exploit the observation that analytical form of conservation laws which does not incorporate constitutive equations is independent of their reversibility properties. This feature, which is equivalent with the statement that the matter tensor compontents are the state functions, allows one to derive the energy–momentum tensor and corresponding conservation laws without the prior knowledge of constitutive or kinetic equations. The associated approach is outlined below.

For the energy density given by Eq. (33) above, the double Legendre transform (38) is

$$\begin{aligned}L(\rho, s, \mathbf{j}_{\mathrm{s}}, \mathbf{J}) = \frac{1}{2}\rho^{-1}\mathbf{J}^2 + \frac{1}{2}\rho^{-1}g\mathbf{j}_{\mathrm{s}}^2 - \rho e^{\mathrm{eq}}(s, \rho) \\ - \rho\psi(\mathbf{x}, t).\end{aligned} \tag{39}$$

To obtain the energy–momentum tensor and related conservation laws, Hamilton's principle in the Eulerian representation of the fluid motion is used. The constraints resulting form the conservation of mass and entropy are taken into account by using the method of Lagrange multipliers, ϕ and η. Hence the following expressions

$$\phi(\mathbf{x}, t)\left(\frac{\partial \rho}{\partial t} + \nabla.\mathbf{J}\right) = 0, \tag{40}$$

$$\eta(\mathbf{x}, t)\left[\frac{\partial \rho s}{\partial t} + \nabla.(\mathbf{J}s + \mathbf{j}_{\mathrm{s}})\right] = 0 \tag{41}$$

are added to the kinetic potential L in the action integral. Here ϕ and η are the field functions describing the Lagrangian multipliers associated with the mass and entropy conservation. The sum $\mathbf{J}s + \mathbf{j}_{\mathrm{s}}$ in Eq. (41) is the total entropy flux composed of the convective part $\mathbf{J}s = \rho\mathbf{u}s$ and the diffusive part $\mathbf{j}_{\mathrm{s}}$. As it is well known, the diffusive flux $\mathbf{j}_{\mathrm{s}}$ is related to the heat flux, but we do not make this assumption in advance. In fact, in this approach, the entropy flux is a more fundamental quantity than the heat flux $\mathbf{q}$. The relativistic invariance of total entropy and the existence of a well-defined relativistic four-vector of the entropy, contrasted with the absence of such properties for the heat flux, support this approach.

In addition to the constraints associated with Eqs. (40) and (41) one more constraint should be taken into account. This is the so-called Lin's [16] constraint preserving the identity of each definite fluid particle. It results in the constancy of the Lagrangian coordinate $\alpha(\mathbf{x}, t)$ of this particle ($\mathrm{d}\alpha/\mathrm{d}t = 0$) along the path. Scalar α can be used in the case of our displacement-free model [17]. Hence the expression

$$\lambda(\mathbf{x}, t)\left(\rho\frac{\partial\alpha}{\partial t} + \mathbf{J}.\nabla\alpha\right) = 0, \tag{42}$$

with the new Lagrangian multiplier $\lambda(\mathbf{x}, t)$ is added to the kinetic potential L. As a result, an action functional is obtained in the form

$$A' = \int\left\{L(\rho, s, \mathbf{J}, \mathbf{j}_s, \mathbf{x}, t) + \phi\left(\frac{\partial\rho}{\partial t} + \nabla.\mathbf{J}\right) + \eta\left[\frac{\partial\rho s}{\partial t} + \nabla.(\mathbf{J}s + \mathbf{j}_s)\right] + \lambda\left(\rho\frac{\partial\alpha}{\partial t} + \mathbf{J}.\nabla\alpha\right)\right\}, \tag{43}$$

which, however, leads to components of the energy–momentum tensor G^{jk} containing the Lagrangian multipliers explicitly. In order to arrive at "physical" components of G^{jk} (without multipliers) expressions (40) and (41) in Eq. (43) are transformed, in the known way, by using the divergence theorem and rejecting four-divergences [18]. This procedure does not affect stationary conditions of the action and yields

$$A = \int\left\{L(\rho, s, \mathbf{J}, \mathbf{j}_s, \mathbf{x}, t) + \rho\left(\frac{\partial\phi}{\partial t} + \mathbf{J}\cdot\nabla\phi\right) + \left[\rho s\frac{\partial\eta}{\partial t} + (\mathbf{J}s + \mathbf{j}_s)\nabla\eta\right] + \lambda\left(\rho\frac{\partial\alpha}{\partial t} + \mathbf{J}\cdot\nabla\alpha\right)\right\}. \tag{44}$$

In the case when $\mathbf{j}_s = 0$ in L and in the η term of Eq. (44) the action functional goes over into that for the Eulerian fluid. It can be shown that the physical meaning of the Lagrangian multipliers remains the same as in the case of the Eulerian fluid, namely ϕ is the velocity potential when the flow is irrotational and at the same time the Lagrangian action of a fluid particle which has the initial velocity λ. The convective derivative of η is just a nonequilibrium temperature T.

The conservation laws are obtained for extended kinetic potential (39) from the basic expression for the energy momentum tensor

$$G^{jk} = \sum_1 \frac{\partial q_1}{\partial\chi^j}\left[\frac{\partial\Lambda}{\partial(\partial q_1/\partial\chi^k)}\right] - \delta^{jk}\Lambda, \tag{45}$$

where δ^{jk} is the Kronecker delta and $\boldsymbol{\chi} = (\mathbf{x}, t)$ comprises the spatial coordinates and time. The first Nöther's theorem yields the invariance conditions for the action $\mathrm{A}[\mathbf{q}(\boldsymbol{\chi})]$ with respect to the parallel translations of space and time coordinates [14]. In absence of external fields these invariance conditions are conservation equations for momentum and energy, yet, when external fields are present, the Lagrangian Λ contains explicitly some of coordinates χ^j. Then only balance equations result. Explicitly they are

$$\sum_k\left(\frac{\partial G^{jk}}{\partial\chi^k}\right) + \frac{\partial\Lambda}{\partial\chi^j} = 0 \tag{46}$$

for $j, k = 1, 2, \ldots, 4$. Eq. (46) is the formulation of balance equations for momentum ($j = 1, 2, 3$) and energy ($j = 4$). In absence of external fields they describe the vanishing four-divergences (div, $\partial/\partial t$) of G^{jk}.

The tensor $\mathbf{G} = G^{jk}$ has the following general structure

$$\mathbf{G} = \begin{bmatrix}\mathbf{T} & -\boldsymbol{\Gamma}\\ \mathbf{Q} & E\end{bmatrix}, \tag{47}$$

where $\mathbf{T}$ is stress tensor, $\boldsymbol{\Gamma}$ is momentum density, $\mathbf{Q}$ is energy flux density, and E is total energy density. The components of this tensor are well known for the adiabatic fluid in which heat flow is absent ("perfect fluid"; [14]). The case of fluids with finite thermal conductivities is most difficult; thus any implications of action (44), which refers to fluids conducting heat ideally, are of interest.

Eq. (44) and its stationarity conditions lead to the extremum Lagrangian in the form

$$\Lambda = P^{\mathrm{eq}}(\rho, s) - \frac{1}{2}(\partial g/\partial\rho)_s\mathbf{j}_s^2 \tag{48}$$

which is the nonequilibrium pressure at point A, Fig. 1. It can be obtained by differentiation of nonequilibrium energy e versus ρ (or v) and keeping constant the entropy s and the thermal momentum $\mathbf{i}_s$ (the "natural" variables of e). Eq. (48) is a generalization of the result known for the equilibrium Eulerian "perfect" fluid without heat, where $\Lambda = P$ in both Newtonian and relativistic cases. With the stationarity conditions of action (44) and Eq. (48), the stress tensor T^α_β follows in the form ($\alpha, \beta = 1, 2, 3$)

$$G^\alpha_\beta = T^\alpha_\beta = -\frac{\partial L}{\partial J^\alpha}J_\beta - \frac{\partial L}{\partial j^\alpha_s}j_{s\beta} - \Lambda\delta^\alpha_\beta = \rho u^\alpha u_\beta - \frac{1}{2}\rho g s^2 v^\alpha_s v_{s\beta} - \delta^\alpha_\beta\left[P^{\mathrm{eq}}(\rho, s) - \frac{1}{2}(\partial g/\partial\rho)_s j_s^2\right]. \tag{49}$$

This theory leads also to the same vector of the momentum density $G^\alpha_4 = -\Gamma^\alpha$ for which one obtains ($\alpha = 1, 2, 3$)

$$-G^\alpha_4 = \Gamma^\alpha = \frac{\partial\phi}{\partial x^\alpha}\rho + \frac{\partial\eta}{\partial x^\alpha}\rho s + \frac{\partial\alpha}{\partial x^\alpha}\rho\lambda = \frac{\partial L}{\partial J^\alpha}\rho = \rho u^\alpha. \tag{50}$$

Thus, the momentum density equals the density of mass flux $\mathbf{J}$.

In the energy representation, the equation of momentum balance resulting from the general formula, Eq. (46) taken for $j = 1, 2, 3,\ k = 1, 2, 3, 4$ and Eqs. (49) and (50), is, in vector notation,

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla .\left(\rho \mathbf{u}\mathbf{u} + \mathbf{I}\left[P^{\mathrm{eq}} - \frac{1}{2}(\partial g/\partial \rho)_{\mathrm{s}}\mathbf{j}_{\mathrm{s}}^{2} \right] + g\rho s^{2}\mathbf{v}_{\mathrm{s}}\mathbf{v}_{\mathrm{s}} \right) - \rho \mathbf{F} = 0. \tag{51}$$

In comparison with Eulerian fluid, the diffusion of heat or entropy results in the appearance of stresses which can exist even if the fluid is at rest ($\mathbf{J} = 0$). This effect is also predicted by Grad's [2] analysis of the Boltzmann equation.

Consider now the vector of the density of energy flux $Q_{\beta} = G_{\beta}^{4}$. Eq. (45) and stationarity conditions of action (44) yield

$$\begin{aligned} -G_{\alpha}^{4} = Q_{\beta} &= -\frac{\partial \phi}{\partial t}J_{\beta} - \frac{\partial \eta}{\partial t}(J_{\beta}s + j_{s\beta}) + \frac{\partial \alpha}{\partial t}J_{\beta}\lambda \\ &= -\frac{\partial L}{\partial \rho}J_{\beta} - \left(\frac{\partial L}{\rho \partial s} - \frac{\mathbf{J}}{\rho}.\frac{\partial L}{\partial \mathbf{j}_{\mathrm{s}}} \right) j_{s\beta}. \end{aligned} \tag{52}$$

Whence, the energy flux for kinetic potential (39) and action (44) is

$$\begin{aligned} Q_{\beta} = \rho u_{\beta}&\left[\frac{1}{2}\rho \mathbf{u}^{2} + h^{\mathrm{eq}} + \psi + \frac{1}{2}gs^{2}\mathbf{v}_{\mathrm{s}}^{2} - \frac{1}{2}(\partial g/\partial \rho)_{\mathrm{s}}\mathbf{j}_{\mathrm{s}}^{2} \right] \\ &- gs(\mathbf{u}.\mathbf{v}_{\mathrm{s}})j_{s\beta} + \left[T - \frac{1}{2}(\partial g/\partial \rho)_{\mathrm{s}}\mathbf{j}_{\mathrm{s}}^{2} \right] j_{s\beta}. \end{aligned} \tag{53}$$

Eqs. (48), (50) and (51) show explicitly effects of nonequilibrium terms. To verify the validity of L we calculate the total energy density $G_{4}^{4} = E$, Eq. (45) for $j = k = 4$, which is

$$\begin{aligned} G_{4}^{4} = E &= -\frac{\partial \phi}{\partial t}\rho - \frac{\partial \eta}{\partial t}\rho s + \frac{\partial \alpha}{\partial t}\rho \lambda - \Lambda \\ &= -\frac{\partial L}{\partial \rho}\rho - \left(P^{\mathrm{eq}} - \frac{1}{2}(\partial g/\partial \rho)_{\mathrm{s}}\mathbf{j}_{\mathrm{s}}^{2} \right). \end{aligned} \tag{54}$$

When L of Eq. (39) is applied in Eq. (54) the result is E consistent with Eq. (38)

$$E = \rho \left(\frac{1}{2}\mathbf{u}^{2} + e^{\mathrm{eq}}(\rho, s) + \frac{1}{2}gs^{2}\mathbf{v}_{\mathrm{s}}^{2} + \psi \right). \tag{55}$$

Thus the true nonequilibrium energy density E, Eqs. (33) or (34), is recovered after using the Legendre transformation of Eq. (38) and kinetic potential (39). The associated energy balance reads

$$\begin{aligned} &\partial \rho \left(\frac{1}{2}\mathbf{u}^{2} + e^{\mathrm{eq}}(\rho, s) + \psi + \frac{1}{2}gs^{2}\mathbf{v}_{\mathrm{s}}^{2} \right) \Big/ \partial t \\ &+ \nabla .\left\{ \rho \mathbf{u}\left[h^{\mathrm{eq}} + \frac{1}{2}\mathbf{u}^{2} + \psi + \frac{1}{2}gs^{2}\mathbf{v}_{\mathrm{s}}^{2} - \frac{1}{2}(\partial g/\partial \rho)_{\mathrm{s}}\rho^{-1}\mathbf{j}_{\mathrm{s}}^{2} \right] \right. \\ &\left. + \left[T^{\mathrm{eq}} - \frac{1}{2}(\partial g/\partial s)_{\rho}\mathbf{j}_{\mathrm{s}}^{2} \right]\mathbf{j}_{\mathrm{s}} + (g\rho^{-1}\mathbf{j}_{\mathrm{s}}\mathbf{j}_{\mathrm{s}}) \cdot \mathbf{u} \right\} - \rho \partial \psi/\partial t = 0. \end{aligned} \tag{56}$$

The recognition of the nonequilibrium variables (e, T, P) as those pertaining to the actual physical state (point A, Fig. 1) makes it possible to express balance equations in terms of these variables. The results are not only simple but also take an "objective" form independent of the representation used. This occurs because the parameters of the reference equilibrium state (B, C or D; Fig. 1) do not appear in the "objective" balance laws. The representation-free form of the balance Eqs. (51) and (56) is, respectively,

$$\frac{\partial_{\rho}\mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u}\mathbf{u} + \mathbf{I}\mathbf{P} + \mathbf{\Pi}) - \rho \mathbf{F} = 0, \tag{57}$$

$$\begin{aligned} &\partial \rho \left(\frac{1}{2}\mathbf{u}^{2} + e(\rho, s) + \psi \right) \Big/ \partial t + \nabla .\left[\rho \mathbf{u}\left(h + \frac{1}{2}\mathbf{u}^{2} + \psi \right) \right. \\ &\left. + T\mathbf{j}_{\mathrm{s}} + \mathbf{\Pi} \cdot \mathbf{u} + \mathbf{\Pi} \cdot \mathbf{v}_{\mathrm{s}} \right] - \rho \partial \psi/\partial t = 0. \end{aligned} \tag{58}$$

All quantities pertain here to point A in Fig. 1. Here $\mathbf{\Pi} = g\rho^{-1}\mathbf{j}_{\mathrm{s}}\mathbf{j}_{\mathrm{s}} = \rho g s^{2}\mathbf{v}_{\mathrm{s}}\mathbf{v}_{\mathrm{s}}$ is the entropy flow contribution to the pressure tensor $\mathbf{P}$ and $\mathbf{\Pi} \cdot \mathbf{u}$ is the related power. Although this form of balance law resembles precisely that known from the description of fluids in local equilibrium, we stress that the quantities e, P and T are here flux dependent. This terms, of course, from the nonequilibrium nature of fluid being considered. Splitting these quantities into the sum of the parts of a reference equilibrium (B, C or D; Fig. 1) and nonequilibrium flux corrections is always representation dependent – the price paid by one who wants to use the well-known equilibrium data in disequilibrium. Thus, whenever the objectivity is not assured, equations of nonequilibrium fluids change their forms depending on variables used, as nonequilibrium corrections appearing in one representation change or vanish in another representation. Yet, as we have already attained the objective or representation-independent form of balance laws, we omit details of comparison of balance laws in various representations.

5. Work limits through statistical and stochastic approaches

Here we deal with the second group of problems, namely, those involving the production of consumption of work in a finite time.

They often occur in practical or industrial devices, where extremum of work is sought for a given state change of a controlled (key) fluid and for a given duration. We consider the controlled fluid which changes its thermodynamic coordinates between two fixed states while interacting all the time with the environment through a sequence of perfect work-producing devices (Carnot thermal machines). Fig. 2 schematizes a sequential work-production process. We assume that we

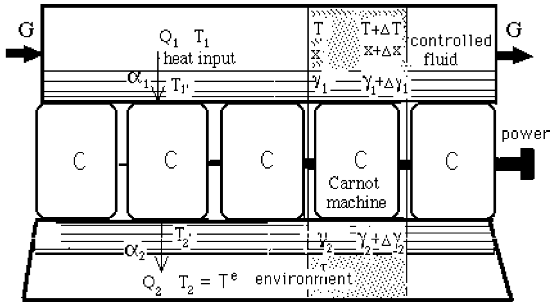

Fig. 2. The scheme of power production in a sequence of infinitesimal Curzon–Ahlborn–Novikov engines.

work with the system without inertial affects. When the duration allowed to accomplish the state change of the controlled fluid is infinite, the extremum work is the change of classical (reversible) exergy. However, when the duration is finite only irreversible process is possible. In this case a generalized or finite-time exergy characterizes properties of extremal work. For continuous process with pure heat transfer a simple formula was found for the finite-time thermal exergy

$$\begin{aligned} E_x(T,T^e,h) &= c(T-T^e) - cT^e \ln\frac{T}{T^e} \pm cT^e\sqrt{\frac{h}{cT^e}}\ln\frac{T}{T^e} \\ &= E_x(T,T^e,0) \pm T^e S_\sigma, \end{aligned} \tag{59}$$

[19]. This corresponds with an infinite number of stages N in Fig. 2. The finite-N counterparts of the formula were also obtained. Here h is an optimal intensity index numerically equal to a hamiltonian, $E_x(T,T^e,0)$ is the classical exergy, and $S_\sigma = \min S_\sigma$ is the minimal entropy production. The upper sign refers to the heat-pump mode in which power is consumed and the lower one to the engine mode in which power is produced. In related work functionals, the irreversibility effect is represented by their broken invariance when the process rate u is replaced by the inverted rate $-u$. Post-thermostatic, rate penalty terms are crucial for work potentials generalized to finite durations. Our results show that the Hamilton–Jacobi–Bellman (HJB) theory is a basic ingredient of the analysis leading to the finite time exergy [19,20].

We discuss here some related statistical issues. The entropy serving to statistical analysis is the information-theoretic entropy, and the modeling of the underlying dynamics involves working with master equations in the probability space. With the statistical theory at hand, macroscopic results can be expressed in terms of the pertinent statistical averages. One may expect that optimal and nonoptimal configurations of the cascade arrangement (defined here macroscopically) can be distinguished due to their statistical properties.

A synthesis of the statistical thermodynamics of Onsager and the kinetic molecular theory of Boltzmann has recently been achieved which may help accomplish the above tasks [15]. This synthesis provides a mechanistic foundation for thermodynamics and thermokinetics. It is based on the idea of elementary molecular processes (indexed by i)

$$(n_{i1}^+, n_{i2}^+, \ldots) \iff (n_{i1}^-, n_{i2}^-, \ldots) \tag{60}$$

with the extensive thermodynamic variables represented by the vector $\langle \mathbf{n} \rangle = (\langle n_1 \rangle, \ldots, \langle n_k \rangle)$. The superscripts + and − refer to the forward and backward steps in generalized reactions. It can be shown that these processes provide a natural description of bimolecular collision dynamics and chemical kinetics. The transition rate of an elementary process, that is the number of times per second that it occurs in the forward or reverse direction, is given by the canonical form

$$V_i^+ = \Omega_i^+ \exp\left(-\sum_1 Y_1^+ n_{i1}/\mathbf{k} \right), \tag{61}$$

and likewise

$$V_i^- = \Omega_i^- \exp\left(-\sum_1 Y_1^+ n_{i1}/\mathbf{k} \right). \tag{62}$$

The constants Ω_i^+ and Ω_i^- are the intrinsic rates of the forward and reverse steps of the elementary process (i) and are the basic transport coefficients in the canonical theory. Y_1 are intensive variables which are functions of the extensive variables; they are the derivatives of a local equilibrium entropy $S(\langle \mathbf{n} \rangle)$. With canonical representation for rates of elementary processes in resistors of CAN stages, one can develop the statistical thermodynamics of molecular processes in a form applicable to systems close or far from equilibrium in which both transport and rate processes can be treated in a unified way, and nonlinear molecular mechanisms can be taken into account.

For systems of CAN type mesoscopic descriptions are in the state of development [21]. In the work adduced the dynamics of the Carnot fluid is a sole effect described by a master equation. However, since the transport law has a considerable effect upon the engine operation, master equations should also describe the dynamics of transfer in resistors. Quantum master equations can be applied, derived from the underlying theory of the system and the coupled reservoirs [21]. The situation is considerably simplified if the off-diagonal terms of the density matrix are eliminated, leading to an analysis based only on the energy-level populations. The first law of thermodynamics has an interesting interpretation in this context: the population transfer from one level to the other is the microscopic manifestation of heat exchange, whereas changing the energy gap between the levels (energy change caused by varying an external field) is associated with work. Consequently, a macroscopic model of CAN cascade can be transformed in a corresponding mesoscopic model. A difficulty arises when the analysis of CAN cascades involves relaxation under the influence of a time-dependent field, where the formulation of thermodynamically coherent master equations is quite a subtle task.

To outline basics of modeling, consider the controlled fluid composed of many noninteracting harmonic oscillators (HO). Ignoring zero-point energy, the energy levels of the HO are $E_n = n\omega$ $(n = 0, 1, 2, \ldots,)$ where ω is the oscillator's frequence in units where modified Planck constant equals 1. The average energy is

$$\langle E\rangle = \sum_0^\infty p_n(t)E_n = \omega\sum_0^\infty p_n(t)n = \omega\langle n\rangle, \tag{63}$$

where $p_n(t)$ is the probability for finding the oscillator in the level n. In the average energy differential, $\mathrm{d}\langle E\rangle = \langle n\rangle\mathrm{d}\omega + \omega\mathrm{d}\langle n\rangle$, the first term is associated with work and the second with heat. If we only allow transitions such that $\Delta n = \pm 1$, the master equation is

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = k_\uparrow np_{n-1} + k_\downarrow(n+1)_{p_{n+1}} - [(k_\downarrow n + k_\uparrow(n+1)]p_n, \tag{64}$$

[22]. Detailed balance corresponds with $k_\uparrow/k_\downarrow = e^{-\omega/kT}$. From the above equation, the differential equation for $\langle n\rangle$ is obtained

$$\langle n\rangle' = \langle n\rangle + \frac{\mathrm{d}\langle n\rangle}{g'\mathrm{d}t}, \tag{65}$$

where $g' = k_\downarrow - k_\uparrow$ and $\langle n\rangle' = k_\downarrow/g' = (\mathrm{e}^{-\omega}/kT - 1)^{-1}$. Eq. (65) preserves Boltzmannian distribution in time. It refers to two macroscopic equations

$$T_1' = T_1 - \frac{\mathrm{d}Q_1}{\mathrm{d}\gamma_1} \tag{66}$$

and

$$\begin{aligned}\mathrm{dQ}_1/\mathrm{d}\gamma \equiv -u &= -\frac{Gc\mathrm{d}T}{\alpha'\mathrm{d}A} = -\frac{\rho vc\mathrm{d}T}{\alpha' a_\mathrm{v}\mathrm{d}x} = -\chi v\frac{\mathrm{d}T}{\mathrm{d}x}\\ &= -\chi\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\mathrm{d}T}{\mathrm{d}\tau}\end{aligned} \tag{67}$$

which are well-known from the standard thermodynamic theory of the process. The consistency condition states that the term $\mathrm{d}Q_1/\mathrm{d}\gamma_1 = (g/g_1)\mathrm{d}Q_1/\mathrm{d}\gamma$ is replaced by $-(g/g_1)\mathrm{d}T/\mathrm{d}\tau$ and $\tau = tg'g/g_1$. See Fig. 2 and related references [19,20]. The basic equation (64) can thus serve as a generalized constraint within the theory in which a unique temperature of the driving nonequilibrium fluid cannot be defined.

Underlying statistical and stochastic approaches should also help understand the role and range of assumptions on which the macroscopic model is based. In fact, similar to other thermodynamic models, even with taking dissipation into account (i.e. making the thermodynamic description closer to reality), the macroscopic model still remains highly abstract, as it still carriers all abstract assumptions of the sequence of elementary engine modules, such as: no heat (mass) fluxes in the x-direction along the series of Carnot engines, which means absence of their mutual interference or the lack of related conductances, and capability of taking work out of such a series of adjacent engine modules. In fact, it is one of typical abstract systems of thermodynamics as many others found in books on applied thermodynamics rather than a definite practical system [10,23,24]). They all serve for evaluation of thermodynamic limits (bounds) on the work released (consumed) from (by) nonequilibrium systems. Yet all models of these systems share an assumption, typical of hydrodynamic level, which states that the fluid flow is represented by motion of artificial fluid particles, treated as small thermodynamics subsystems, which compose altogether the whole fluid. It is then assumed that in macroscopic modeling – which applies purely thermodynamic quantities – the size of each elementary module, while small ('differential') with respect to the whole sequence, must be large enough in comparison to sizes of all microobjects (molecules), and that the molecular chaos takes place, thus making possible definitions of thermodynamic parameters such as temperature, internal energy, etc. in terms of pertinent statistical averages.

6. Evolution of multistate living systems by information-theoretic entropy

Models of development of multistage systems can successfully mimic some processes of biological development and evolution, whereas the information-theoretic entropy can successfully be used to measure changes in their statistical properties. The so-called Wilinston's law is often quoted in the evolution literature, which states that for an organism possessing many of the same or similar elements, a tendency appears to reduce the number of these elements along with the simultaneous modification (specialization) of these elements which are saved by the organism. Saunders and Ho [25,26]) recall that the evolution leading from the trylobite to crab is a suitable example illustrating this tendency. It should be kept in mind that annelids, ancestors of trilobite, live today, and crabs, their mutants or peculiar descendants in the evolutionary process, live today as well. Trilobites became extinct in perm (270–220 millions of years ago) in camber, and the problem of their extinction calls for explanation. Szwast [3] has investigated evolution from trilobite (as an organism with many states: segments and pairs of legs) to crab, with far fewer of each and with one pair of legs modified (specialized) into claws. The basic problem was: why extra states (pairs of legs) evolved and what was the cause of trilobites extinction. His mathematical model of the evolution implies that the increase of number of states (pairs of legs) is governed by extremum gradient of a potential which may be either the information entropy or a complexity function, as each of these quantities increases with number of states in the system. On the other hand, as shown by Szwast, a decrease of number of states (pairs of legs) seem to result from catastrophes on the trajectory of evolution, as the modification (specialization) leads evolution to a catastrophe region. What evolution criterion should actually be preferred is the subject of current investigations; according to Saunders and Ho the principle of minimum increase holds for complexity function rather than for entropy. However, as shown below, a related extremality analysis can be developed for an arbitrary potential function [27].

Szwast's [3] description of evolution involves calculations of information entropy, $S = -\sum p_i \ln p_{i,}$ where the summation is over the number of states. Here p_i is the probability of finding an element in the state i among n states possible and the sum $\sum p_i = 1$. Maximum of unconstrained entropy appears for the total randomness. In this case $p_i = 1/n$, for n states, and $S_{\max} = -n(1/n)\ln(1/n) = \ln n$. In the trilobite analysis, however, the number of states is $2n+1$ ($2n$ legs and the rest part of the body); thus $S_{\max} = \ln(2n+1)$. Moreover, it was only recently explained that entropy itself is not a direct measure of disorder for growing systems as it is an extensive quantity [28]. In other words, for growing systems the classical definitions of disorder $D = \mathrm{e}^{S}$ and order $\Omega = \mathrm{e}^{-S}$ proposed by Schrödinger [29] are inapplicable. Their flaws are not shared by Landsberg's definitions of disorder and order. According to Landsberg, disorder $D = S/S_{\max}$ and order $\Omega = 1 - D$. As $S_{\max}$ depends on n, in Landsberg's definition, both disorder D and order Ω are functions of entropy S and number of states in the system, n; i.e. $D = D(S, n)$ and $\Omega = W(S, n)$. For evolution processes the particularly important role is played by the complexity Γ, which is a function of disorder D and order Ω, i.e. $\Gamma = f(D, \Omega)$. In the literature various functions f were advocated. A frequent form has the simple structure $\Gamma = 4D\Omega = 4D(S, n)[1 - D(S, n)]$, which was used by Szwast [3]. In this case the maximum of Γ is attained for $D = 0.5$ and equals the unity.

The basic statement of Saunders and Ho [26] "Only completely reversible changes are processes which undergo without change of complexity" was successfully applied in Szwast's [3] analysis. This application requires constancy of complexity or entropy (motions along "entropy isolines") when modifications or specializations occur at a constant number of states, n. In other words, the decrease of states (pairs of legs) is a possible process which is compensated during evolution by the creation of modified states (claws), the process which occurs along an isoline of entropy. This entropy is not a maximum entropy for a given n; it is rather the entropy which maximizes complexity Γ (in fact, probabilities which would maximize entropy would rather minimize complexity). Therefore, it is the set of conditions $\mathrm{d}\Gamma/\mathrm{d}S = 0$ and $\mathrm{d}^2\Gamma/\mathrm{d}S^2 < 0$, which define the entropy isoline along which modification or specialization of an organism is possible. In this model, the complexity-maximizing entropy follows as S_n^{opt} or $\hat{S}_n = (1/2)$ $S_n(\max)$, and the corresponding complexity $\Gamma_n = 1$. Both the maximal entropy (at the complete randomness), and the one which maximizes complexity ($\hat{S}_n$ or one half of $S_n(\max)$) are increasing functions of the number of states, n.

In Szwast's [3] evolution description, a map of possible states was obtained in the form of entropy isolines. Evolution of states towards a crab refers to a situation in which an organism with one pair of states (legs) is modified (specialized) along a reversible path. With the normalization condition incorporated to eliminate p_2, the probability attributed to one pair of states (legs), the entropy isoline along which the specialization proceeds has an equation $V_n(p_0, p_1) \equiv S_n(p_0, p_1) = \hat{S}_n$.

Fig. 3 gives the qualitative description of trajectories of reversible modification (specialization) of one pair of original states (legs) for various values of variable n, which constitutes the sum of $n-1$ identical pairs of states (legs) and one pair being modified. Dots on trajectories mark findings for organisms without specialization of states (legs); thus they refer to organisms possessing n pair of identical states (legs).

The following question arises: why an organism possessing n of identical pair of states (legs) tends to the state associated with $n+1$ pair of legs during the evolution, or, why the evolution proceeds in the direction of an increase of identical states ? [3]. The results below imply that it is the shortest line between the dot point on the curve n and the curve $n+1$ which deter-

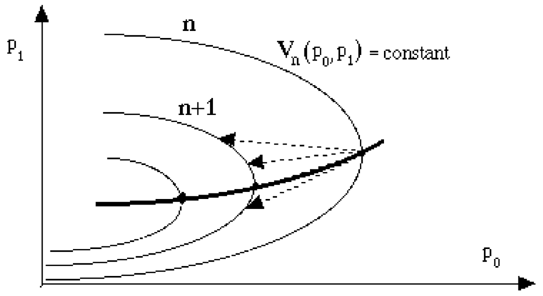

Fig. 3. A minimum distance problem between a dot point on isoline n and the isoline $n+1$. In the evolution analysis, isolines are paths of the reversible modification of single pair of states (legs) for various n, where n is the sum of $n-1$ pairs of the same states (legs) and one modified pair.

mines the location of the dot point on the curve $n+1$. The considerations below substantiate this statement with the help of the optimal control theory.

7. Potential principle of extremality as a driving force of evolution dynamics

The extremality analysis can be developed for an arbitrary potential function [27]. Let us introduce the function

$$F_n(p_0, p_1) = V_n(p_0, p_1) - \widehat{V}_n = 0, \tag{68}$$

where $\widehat{V}_n$ is the constant value of V_n along the isoline of potential V. The numerical value of the function F_n equals zero for all states corresponding with the complexity-maximizing entropy. These are states located on "reversible isolines" of Fig. 3, for various n. The total differential of F is the differential of potential V restricted to values $V_n(p_0, p_1)$ satisfying (68)

$$\begin{aligned} \mathrm{d}F_n(p_0, p_1) &= \mathrm{d}V_n(p_0, p_1) \\ &= \frac{\partial V_n(p_0, p_1)}{\partial p_0}\mathrm{d}p_0 + \frac{\partial V_n(p_0, p_1)}{\partial p_1}\mathrm{d}p_1 = 0. \end{aligned} \tag{69}$$

The direction coefficient of the tangent to each of the lines $V_n(p_0, p_1)$ is the derivative $v \equiv (\mathrm{d}p_1/\mathrm{d}p_0)_n$. With Eq. (69) this derivative can be determined in terms of the partial derivatives V_n or F_n as

$$v_n \equiv \left(\frac{\mathrm{d}p_1}{\mathrm{d}p_0}\right)_n = -\frac{\partial V_n(p_0, p_1)}{\partial p_0} \bigg/ \frac{\partial V_n(p_0, p_1)}{\partial p_1}. \tag{70}$$

To predict the location of the dot point on the curve $n+1$ when the dot point on the curve n is given, consider the variational problem of the shortest line between the dot point on the curve n and the curve $n+1$. This corresponds with the minimum of a length functional

$$J = \int_{p_0^n}^{p_0^{n+1}} a(p_0)\sqrt{(1 + \left(\frac{\mathrm{d}p_1}{\mathrm{d}p_0}\right)^2}\mathrm{d}p_0, \tag{71}$$

where a "conformal coefficient" $a(p_0)$ takes into account the deviation from the Euclidean measure of length. It was assumed here that only basic part of the body (with the probability p_0) influences the value of the coefficient a. The integrand of this Lagrangian functional is designated by L. The general Euler–Lagrange equation for the minimum of J is

$$\frac{\partial L}{\partial p_1} - \frac{\mathrm{d}}{\mathrm{d}p_0}\left(\frac{\partial L}{\partial(\mathrm{d}p_1/\mathrm{d}p_0)}\right) = 0 \tag{72}$$

and, for the considered model, it has the form

$$\frac{\mathrm{d}}{\mathrm{d}p_0}\left(\frac{\mathrm{d}p_1/\mathrm{d}p_0}{\sqrt{1 + (\mathrm{d}p_1/\mathrm{d}p_0)^2}}\right) = 0. \tag{73}$$

This corresponds to Euclidean metrix and – if $a = 1$ – to the Euclidean distance. In a more general case, when the coefficient a in Eq. (71) depends on all probabilities, the problem can be stated as a geodesics problem.

The solution of Eq. (73) describes the family of the straight lines

$$p_1 = C_1 p_0 + C_2 \tag{74}$$

which are extremals in the flat space.

Any extremal which starts from the dot point on the curve n and terminates on the curve $n+1$ should satisfy the transversality condition [30]

$$\begin{aligned} \delta J &= \left\{L - \frac{\partial L}{\partial(\mathrm{d}p_1/\mathrm{d}p_0)}(\mathrm{d}p_1/\mathrm{d}p_0)\right\}\delta p_0 \\ &\quad + \left(\frac{\partial L}{\partial(\mathrm{d}p_1/\mathrm{d}p_0)}\right)\delta p_1 \\ &= 0, \end{aligned} \tag{75}$$

where variations δp_0 and δp_1 are linked by condition (70) applied for the curve $n+1$

$$\left(\frac{\delta p_1}{\delta p_0}\right)_{n+1} = -\frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} \bigg/ \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1}. \tag{76}$$

This assures optimal location of the final point on the curve $n+1$. For any J which has meaning of a length, Eq. (75) describes the condition for the length extremum of the extremal which starts from the dot point on the curve n and terminates on the curve $n+1$. Assuming arbitrary free variations of p_0 and substituting variation δp_1 from Eq. (76) into Eq. (75) yields the condition

$$\begin{aligned} &L - \frac{\partial L}{\partial(\mathrm{d}p_1/\mathrm{d}p_0)}\Bigg((\mathrm{d}p_1/\mathrm{d}p_0)_{n+1} \\ &\quad + \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} \bigg/ \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1}\Bigg) \\ &\quad \equiv L - \frac{\partial L}{\partial(\mathrm{d}p_1/\mathrm{d}p_0)}(u_{n+1} - v_{n+1}) = 0. \end{aligned} \tag{77}$$

Condition (77) links two slope coefficients, $u_{n+1} = \mathrm{d}p_1/\mathrm{d}p_0$ or the tangent to the extremal of integral J and v_{n+1} or the tangent to the isoline $V_{n+1}(p_0, p_1) = \widehat{V}_{n+1}$, Eq. (70), at the optimal end point where the extremal reaches the curve $n+1$. For our Lagrangian L, the above condition takes the form

$$\begin{aligned} &a(p_0)\left\{\sqrt{(1 + u_{n+1}^2)} - \frac{u_{n+1}}{\sqrt{(1 + u_{n+1}^2)}}(u_{n+1} - v_{n+1})\right\} \\ &\quad = 0. \end{aligned} \tag{78}$$

In fact, we observe here the case of Euclidean geometry: conformal coefficient $a(p_0)$ does not change the resulting transversality condition, which is the same in the case when $a = 1$ and when a is arbitrary function, $a(p_0)$. Eq. (78) can be simplified to the form

$$u_{n+1} = -\frac{1}{v_{n+1}} \tag{79}$$

which describes orthogonality of the slopes u_{n+1} and v_{n+1}. From Eqs. (70) and (79),

$$\left(\frac{\mathrm{d}p_1}{\mathrm{d}p_0}\right)_{n+1} = \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1} \Big/ \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} \tag{80}$$

which implies the gradient dynamics for change of probabilities with time in the form

$$\left(\frac{\mathrm{d}p_0}{\mathrm{d}t}\right)_{n+1} \Big/ \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} = \left(\frac{\mathrm{d}p_1}{\mathrm{d}t}\right)_{n+1} \Big/ \frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1} = \omega. \tag{81}$$

The frequency-type coefficient ω has interpretation of a kinetic constant governing the state modification process. While Eq. (81) refers to the simplest metric $g^{ik} \equiv \delta^{ik}$, its tensor generalization can easily be obtained for arbitrary g^{ik} and, in particular, to an arbitrary function $a(p_0, p_1)$ in Eq. (71). Taking into account that our notation deals with probabilities indexed by subscripts, it will be the easiest to treat all independent probabilities as covariant coordinates. To attain the tensor generalization, we transform Eq. (81) to another (primed) coordinate frame which may be curvilinear. We find

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \frac{\partial \mathbf{p}}{\partial \mathbf{p}'}\frac{\mathrm{d}\mathbf{p}'}{\mathrm{d}t} = \omega\frac{\partial V}{\partial \mathbf{p}} = \omega\frac{\partial \mathbf{p}'}{\partial \mathbf{p}}\frac{\partial V}{\partial \mathbf{p}'} \tag{82}$$

whence

$$\frac{\mathrm{d}\mathbf{p}'}{\mathrm{d}t} = \omega\left(\frac{\partial \mathbf{p}'}{\partial \mathbf{p}}\right)\left(\frac{\partial \mathbf{p}'}{\partial \mathbf{p}}\right)\left(\frac{\partial \mathrm{V}}{\partial \mathbf{p}'}\right) = \omega\mathbf{g}^{-1}\left(\frac{\partial \mathrm{V}}{\partial \mathbf{p}'}\right), \tag{83}$$

where $\mathbf{g}^{-1}$ is the matrix of the contravariant metric tensor. The corresponding matrix of covariant metric tensor is then $\mathbf{g}$. We can now ignore primes and write down the obtained result in following tensor form

$$\frac{\mathrm{d}p_i}{\mathrm{d}\tau} = g_{\mathrm{ik}}\left(\frac{\partial V}{\partial p_k}\right), \tag{84}$$

where the nondimesional tine $\tau = \omega t$. The product of the covariant metric tensor g_{ik} and the contravariant gradient vector $\partial V/\partial p_k$ is the covariant gradient vector, $\partial V/\partial p^k$. Thus Eq. (84) states that the covariant rate $\mathrm{d}p_i/\mathrm{d}\tau$ is equal to the covariant gradient vector, $\partial V/\partial p^k$.

In the generalized case considered, an associated discrete dynamics, which describes the passage of the system from the state $\mathbf{p}(n)$ to the state $\mathbf{p}(n+1)$, can be written in the Onsager-like form

$$p_0(n+1) - p_0(n) = \mathscr{L}_{11}\frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} + \mathscr{L}_{12}\frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1}. \tag{85}$$

$$p_1(n+1) - p_1(n) = \mathscr{L}_{21}\frac{\partial V_{n+1}(p_0, p_1)}{\partial p_0} + \mathscr{L}_{22}\frac{\partial V_{n+1}(p_0, p_1)}{\partial p_1}, \tag{86}$$

where $\mathscr{L}_{ik} = g_{ik}\Delta\tau$. In this model each single stage number is identified with the change in the number of state coordinates (legs) by one unit. The discrete nature of dynamical equations in processes of biological development and evolution was recently postulated as a most relevant feature which is characteristic of evolution processes with births, deaths or modifications [31]. The applicability of the above set can be extended by assumption that the starting point at the nth isoline is not necessarily the dot point; with this extension the dynamics generated by Eqs. (85) and (86) covers the whole probability space in which it is represented by trajectories orthogonal to the isolines of the potential. A detailed explanation of the mechanism of state catastrophes, based on this model and bistability and Schlögl's mechanism [32] is in progress. While many of results obtained in this context can only be qualitative in view of different definitions of complexity [33], combining the results of contemporary theory of thermodynamic metric with some numerical tests of evolution can improve the situation. In particular, geometrical measures for energy and entropy changes are known [7,34–39,9,40–46]. Equivalence of statistical and phenomenological metrices is an important issue [9,47]). Extensions to local-nonequillibrium systems are in progress [48–50]). A review on geometrical methods in thermodynamics has recently appeared [51].

8. Final remarks

We have shown the reality of expectation that nonequilibrium thermodynamic ensembles will follow in the future analyses from certain statistical extremum principles in a similar way as ensembles of equilibrium thermodynamics emerge at the present time [52–56]). Main extremum formulations expose action-based and entropy production-based extremum principles for processes without work flow [14,13] and with work flow [24]. Concept of Lagrangian coordinate for energy or entropy has proved its usefulness especially in the context of extremum principles of the action type. The role of extremum principles of minimum entropy-production type increases in view of fact that they generalize some basic findings of equilibrium statistical mechanics, for example, they interpret Lagrange multipliers of conservation laws as nonequilibrium temperature and Planck potentials. At the local equilibrium limit convergence of these nonequilibrium quantities to usual T and μ/T takes place [13], the result confirmed in the framework of Liu's method of Lagrange multipliers [57,58]). For precise definition of local equilibrium in case of reacting systems see the book by Lawton and Kingsburg [59]. Note, however, that in some examples discussed here classical thermodynamic quantities need not be introduced. On the other hand, equations of extremal variational processes are always Hamiltonian (or they can be broken down to a Hamiltonian form). Wave fronts and trajectories are two basic entities associated with such equations.

Besides of the above main formulations, there are also numerous extremum statements for other sorts of problems. These are: variational formulations for transport coefficients [60–64], variational settings for dynamics described by master equation [65–67]), those which involve Kullback's [68] relative information; those for variational derivation of Boltzmann equation [69], and those associated with molecular dynamics methods [70–72]). The entropy principle of extremality, consistent with the above findings, was applied in these works in several different contexts, such as: relation of the second law to the power conversion of energy fluctuations [73], stochastic dynamics described by Fokker–Planck equation related to a master equation for probabilities [67], deterministic dynamics for reacting fields [13], and Finslerian geometries of physical systems [74,75]).

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