PHYSICAL REVIEW A VOLUME 40, NUMBER 1 JULY 1, 1989

Conservation laws from Hamilton's principle for nonlocal thermodynamic equilibrium fluids with heat flow

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(Received 13 February 1989)

Extended thermodynamics of heat-conducting fluids is used to give explicit formulas for nonequilibrium energy density of ideal gas expressed as functions of classical variables and the diffusive entropy flux (a nonequilibrium variable). A Lagrangian density associated with the energy density is used to obtain the components of energy-momentum tensor and corresponding conservation laws on the basis of Hamilton's principle of stationary action and Noether's theorem. The heat flux appears naturally as a consequence of a free entropy transfer (independent of mass transfer) and a momentum transport is associated with tangential stresses resulting from this entropy transfer. The compatibility of the present description with the kinetic theory is shown. Hamilton's principle is extended so that the flux of entropy as well as the fluxes and densities of mass are varied independently. The concept of thermal momentum as the derivative of the kinetic potential with respect to the entropy flux is introduced; this quality plays a fundamental role in the extension of Gibbs's equation to describe a nonequilibrium fluid with heat flux.

I. INTRODUCTION

The hydrodynamic laws of conservation of energy and momentum for fluids can be obtained either from kinetic theory,[1-7] by exploiting conservation of the collision invariants, or by using the hydrodynamic variational principle of stationary action.[2,5,8] In the last case, the integrand of the action functional contains the so-called kinetic potential taken conventionally as the difference between the kinetic and static energy of the fluid. When such a definition of L is used, the resulting conservation equations for momentum and energy describe the so-called Eulerian fluid in which the heat concept does not appear ("perfect fluid"). This fact renders the variational approach considerably more restrictive then the kinetic-theory approach in which heat and viscosity appear naturally. Starting from a thermodynamic standpoint we know, however, that a disequilibrium distribution of states (with heat) must have higher availability than the equilibrium one. Therefore, we presume that the restrictive capability of the variational approach is connected with too simplified a form of the kinetic part of L, or, more specifically, with the neglect of some extra availability term in the kinetic part of L. This term is connected with the maximum work obtained during reversible relaxation of the (unconstrained) heat or entropy flux toward isentropic equilibrium. (In most typical, purely irreversible situations this availability is dissipated as the "uncompensated" heat). In this paper we show that if extra availability is taken into account in the action functional then the conservation laws obtained from the stationary action principle contain heat flux and become compatible with those obtained from the kinetic theory to within the accuracy of the viscosity-related terms associated with the fluid velocity gradient neglected here. (In the presence of such terms the usual definition of the conductive entropy flux is questionable[1,6] and we will therefore restrict ourselves to the pure heat-flow case where the quality $\mathbf{j}_s = \mathbf{q}T^{-1}$ is well established.) Some small viscosity-related terms associated with the gradients of $\mathbf{j}_s$ or $\mathbf{q}$ rather than the gradients of $\mathbf{u}$ will survive.[6] It is interesting to note that the proof of the compatibility mentioned above requires a rather unexpected reasoning about the connection between the energy and entropy representations of thermodynamics in the case of nonequilibrium. By establishing this compatibility we arrive at our three principal conclusions. The first is that Hamilton's principle can be extended to systems with heat flow, provided that an appropriate Legendre transformation is used to represent the passage from the nonequilibrium energy to the kinetic potential L. This transform involves not only the usual momentum of unit mass $\mathbf{u}$ related to the mass flux $\mathbf{J}$, but also a thermal momentum variable related to the diffusive entropy flux $\mathbf{j}_s$.

Our second conclusion resolves the mystery of the so-called "kinetic terms" that are in turn appearing and vanishing in various forms of extended thermodynamic theory[1,4,7] and which were thus occasionally criticized as doubtful or simply invalid. It turns out that some kinetic terms which appear in the entropy representation vanish in the energy representation and conversely, and that this effect is connected with the difference between the equilibrium states which are associated with the two kinds of information: the first is related to the energy representation, and the second to the entropy representation of a nonequilibrium system. While this result seems to be of importance for foundations of nonequilibrium thermodynamics, its discussion here is restricted to those facts which are necessary to accomplish the basic purpose of this work, namely, to extend the field form of Hamilton's principle to fluids with heat flow and to show the compatibility of the resulting nonrelativistic energy-momentum tensor with the well-known outcomes of the kinetic theory.[6]

Our third conclusion is that invariance of the stationary Lagrangian Λ and the components of the energy-momentum tensor G^{jk}, with respect to transformation of thermodynamic variables, provides a powerful method to identify unambiguous nonequilibrium temperatures, pressures, and chemical potentials in Λ and G^{jk}, which then leads to an extended (nonequilibrium) Gibbs equation with the "thermal momentum" $\mathbf{i}_s = \partial L / \partial \mathbf{j}_s$ as the fundamental nonequilibrium variable.

The structure of the paper is as follows. In Secs. II and III we use some known results from thermodynamics and nonequilibrium statistical mechanics, see, e.g., Lebon,[1] which allow one to evaluate nonequilibrium entropies and energies off, but not far from Gibbs's equilibrium surface. The expressions obtained are functions of the classical state variables and nonequilibrium variables such as heat flux. Next (Secs. IV and VI), by going to an extended kinetic potential L, we use these results to reach our first objective, to construct a variational formalism describing the reversible behavior of one-component nonequilibrium fluids with heat flow, thereby extending the well-known variational approach to the hydrodynamics of equilibrium (Eulerian) fluids.[2] The construction of the energy-momentum tensor and related balance equations (via Noether's theorem, Sec. VII), allows us to construct a bridge between an Eulerian fluid, for which the heat concept is absent, and the fluid with heat flow, for which the classical and extended nonequilibrium thermodynamic descriptions hold, respectively, the sense of de Groot and Mazur[3] and of Cattaneo.[4] The proof of the relevancy of the thermal momentum variable, the Gibbs equation, the compatibility of our results with those of kinetic theory, and the conclusions (Secs. VIII–X) end the essential body of the paper. Having the balance equations for momentum and energy, we can pass to irreversible processes (Appendix) and ask about the kinetic equation describing the irreversibility of heat flow implied by the positivity of the entropy generation. We show that the resulting theory describing the irreversible heat conduction incorporates Cattaneo's generalization[4] of Fourier's law into the context of the conservation laws,[3] which we obtain by extending Salinger and Whitham's approach.[5] The coefficients in the conduction equation for the ideal gas are also those obtained from kinetic theory.[6,7] In view of this equivalence, the novelty of the paper is partly methodological; we accomplish the extension of Hamilton's approach to the nonequilibrium fluids in the context of recent thermodynamic findings[1,7,9] and formulate the theoretical argument as a field theory[10,11] to be able to use Noether's theorem. The theorem allows us to state and then solve the important problem of an exact form of the energy-momentum tensor for a *nonequilibrium* fluid with heat, which has been unsolved so far in spite of many works done in extended nonequilibrium thermodynamics.[12] But beyond these, the work also lends improved precision to the theory of nonequilibrium temperatures, pressures, and Gibbs's equation, as well as to the theory of non-Fourier heat conduction,[1,4,7] giving an interpretation of the extended thermodynamic force for heat transfer in terms of the Lagrangian (see Appendix). The duality of energy and entropy representations of the thermodynamics and the notion of thermal momentum are developed here for nonequilibrium processes. It is believed that the method presented here will provide a way to extend the well-known results of the Eulerian fluid theory[2,5,8,13,14] to other examples involving nonequilibrium fluxes.

II. THERMODYNAMICS OF HEAT FLOW WITHOUT LOCAL EQUILIBRIUM

We work in the framework of extended thermodynamics of fluids.[1,4,7] 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 an element of a particular fluid, 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 $\tilde{\rho}\tilde{e}$ of the fluid or its specific energy $\tilde{e}$ is a function of the fluid density $\tilde{\rho}$, specific entropy $\tilde{s}$, and diffusive entropy flux $\mathbf{j}_s$, the relaxing variable. The equilibrium

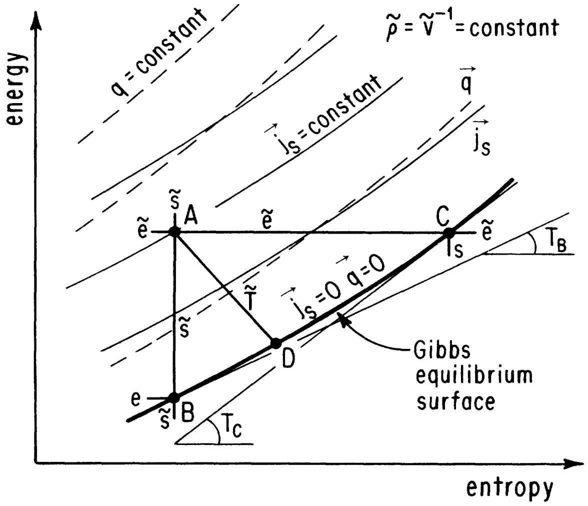

FIG. 1. Three various equilibrium states at the points B, C, and D corresponding to the energy, entropy, and free-energy representations, respectively, for the definite nonequilibrium state, point A. An observer, knowing $\tilde{\rho}$ and $\tilde{e}$ (from an experiment or a computation), formulates his thermodynamic description of the state A in terms of the equilibrium parameters at C for the arbitrary set of nonequilibrium variables (here $\mathbf{j}_s$ or $\mathbf{q}$). However, one who knows $\tilde{\rho}$ and $\tilde{s}$ (e.g., from distribution function $\tilde{f}$ corresponding to A) bases his equation 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 its nonequilibrium variables, whereas the kinetic-theory view corresponds to tracking with C and its variables. The transition from one view to the other is achieved by using Eqs. (93)–(96).

internal energy density ρe of a stable system is the minimum of $\widetilde{\rho e}$ with respect to unconstrained relaxing $\mathbf{j}_s$ at constant $\tilde{\rho}$ and $\tilde{s}$. As $\tilde{\rho}=\tilde{v}^{-1}$, the specific volume, the minimum of $\widetilde{\rho e}$ (or $\tilde{e}$ itself) with respect to $\mathbf{j}_s$ occurs at constant specific entropy $\tilde{s}$ and volume $\tilde{v}$ which are the proper variables at which the energy attains extremum at equilibrium, as known from classical thermodynamics.[9] Since $\mathbf{j}_s$ is a diffusive flux, the minimum occurs at $\mathbf{j}_s=\mathbf{0}$.

In the absence of an external magnetic field the rotation of the system does not change the form of the nonequilibrium function $\tilde{e}(\tilde{s},\tilde{\rho},\mathbf{j}_s)$ which depends then only on the length of the vector $\mathbf{j}_s$; compare the kinetic-theory expression, e.g., (24) below. The following is the McLaurin expansion of $\tilde{e}$ with respect to $\mathbf{j}_s$ in the vicinity of equilibrium ($\mathbf{j}_s=\mathbf{0}$):

$$\tilde{e}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=e(\tilde{s},\tilde{\rho},\mathbf{0})+\tfrac{1}{2}(\partial^2\tilde{e}/\partial\mathbf{j}_s^2)_{\tilde{s},\tilde{\rho}}\mathbf{j}_s^2+O(\tilde{s},\tilde{\rho},\mathbf{j}_s)\ , \tag{1}$$

where

$$\tilde{e}(\tilde{s},\tilde{\rho},\mathbf{0})=e(\tilde{s},\tilde{\rho}) \tag{2}$$

is the equilibrium function of specific energy well known in thermostatics. Since $(\partial\tilde{e}/\partial\mathbf{j}_s)_{\tilde{\rho},\tilde{s}}=0$ at equilibrium, the first-order term disappears from the expansion (1), and the first nonvanishing nonequilibrium term is the term quadratic with respect to $\mathbf{j}_s$. This notion pertains, of course, to any variable that vanishes at equilibrium. It has to be remembered that the second derivative $(\partial^2\tilde{e}/\partial\mathbf{j}_s^2)$ in Eq. (1) is determined at constant $\tilde{s}$ and $\tilde{\rho}$ 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 too 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

$$\tilde{e}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=e(\tilde{s},\tilde{\rho})+\Delta\tilde{e}(\tilde{s},\tilde{\rho},\mathbf{j}_s)\ , \tag{3}$$

where

$$\Delta\tilde{e}=\tfrac{1}{2}(\partial^2 e/\partial\mathbf{j}_s^2)\mathbf{j}_s^2+O(\tilde{s},\tilde{\rho},\mathbf{j}_s) \tag{4}$$

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

From Eq. (3) the following general equation for the perfect differential of $\tilde{e}$ is deduced:

$$\begin{aligned} d\tilde{e}=d(e+\Delta\tilde{e})&=(\partial e/\partial\tilde{s}+\partial\Delta\tilde{e}/\partial\tilde{s})d\tilde{s}\\ &\quad+(\partial e/\partial\rho)+\partial\Delta\tilde{e}/\partial\tilde{\rho})d\tilde{\rho}+(\partial\Delta\tilde{e}/\partial\mathbf{j}_s\cdot d\,\mathbf{j}_s)\\ &=[T(\tilde{s},\tilde{\rho})+\Delta\tilde{T}(\tilde{s},\tilde{\rho},\mathbf{j}_s)]d\tilde{s}+\tilde{\rho}^{\,2}[P(\tilde{\rho},\tilde{s})\\ &\quad+\Delta\tilde{P}(\tilde{\rho},\tilde{s},\mathbf{j}_s)]d\tilde{\rho}+\mathbf{a}_s(\tilde{s},\tilde{\rho},\mathbf{j}_s)\cdot d\,\mathbf{j}_s\ . \end{aligned} \tag{5}$$

Equation (5) defines the corrections $\Delta\tilde{T}$ and $\Delta\tilde{\rho}$ which should be added to $T(\tilde{\rho},\tilde{s})$ and $P(\tilde{\rho},\tilde{s})$ to obtain the proper values of the derivatives $\partial\tilde{e}/\partial\tilde{s}$ and $\partial\tilde{e}/\partial\tilde{\rho}$, Eqs. (8) and (9). In the so-called energy representation of thermodynamics,[15] the space spanned by $\tilde{s}$ and $\tilde{\rho}$ 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 thermodynamics variables used; see, e.g., points C and D in Fig. 1 for isoenergetic ($\tilde{e}=$const) 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, $T_{(B)}$, $P_{(C)}$, etc., will be used or the variables of definite representations will be specified. Where there is no ambiguity, the tilde on symbols $\tilde{T}$, $\tilde{P}$, etc., will be sufficient to describe conventional thermodynamic variables for a nonequilibrium state and bare symbols for the equilibrium state. From Eq. (5) one obtains the quantities

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

$$\tilde{P}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=P(\tilde{s},\tilde{\rho})+\Delta\tilde{P}(\tilde{s},\tilde{\rho},\mathbf{j}_s)\ . \tag{7}$$

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 $\tilde{\rho}$ and $\tilde{s}$, namely,

$$\tilde{T}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=(\partial\tilde{e}/\partial\tilde{s})_{\rho,\mathbf{j}_s}\ , \tag{8}$$

$$\tilde{P}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=\tilde{\rho}^{\,2}(\partial\tilde{e}/\partial\tilde{\rho})_{\tilde{s},\mathbf{j}_s}=-(\partial\tilde{e}/\partial\tilde{v})_{\tilde{s},\mathbf{j}_s}\ . \tag{9}$$

The last quantity defined above in Eq. (5) is the vector variable $\mathbf{a}_s(\tilde{s},\tilde{\rho},\mathbf{j}_s)$ adjoint with respect to the entropy flux $\mathbf{j}_s$ such that

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

We will also use the entropy flux adjoint based on the energy of unit volume $\Delta\widetilde{\rho e}$,

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

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 (Sec. VIII). Restricted to the quadratic approximation of $\Delta\tilde{e}$ in Eq. (4) (the case of small flux $\mathbf{j}_s$) on the basis of Eqs. (3) and (6)–(9), the "nonequilibrium corrections" $\Delta\tilde{T}$ and $\Delta\tilde{P}$ caused by the presence of the flux $\mathbf{j}_s$ are

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

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

i.e., they are homogeneous quadratic functions of the flux $\mathbf{j}_s$. The entropy flux adjoint $\mathbf{i}_s$ is then

$$\mathbf{i}_s=(\partial^2\Delta\widetilde{\rho e}/\partial\mathbf{j}_s^2)^{\mathrm{eq}}\mathbf{j}_s\ . \tag{13}$$

In Eqs. (11)–(13) the equilibrium superscript means that the corresponding derivatives are evaluated at $\mathbf{j}_s=\mathbf{0}$. Therefore, the coefficients of $\mathbf{j}_s$ in Eqs. (11)–(13) depend on the classical variables $(\tilde{s},\tilde{\rho})$ exclusively, so long as the expansion (4) with the expansion about 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 that we are going to investigate. If, however, the thermodynamic space is spanned by the $\tilde{e}$, $\tilde{\rho}$, and **q**-vector variables, one naturally uses the entropy representation.[12,15] By considering the expansion of the entropy around an isoenergetic equilibrium with respect to unconstrained flux **q** (or $\mathbf{j}_s$) one can obtain the formalism analogous to that presented here in energy representation. The corresponding formulas 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[16,17] or equivalent probability distance,[18] increases with the distance of the state A from the Gibbs surface. This distance can be measured in terms of the modulus of the flux $\mathbf{j}_s$ or in terms of the module of the excesses $\Delta\tilde{e}=\overline{AB}$ or $\Delta\tilde{s}=\overline{AC}$. When the curvature of the Gibbs surface can be neglected, corresponding to the near-equilibrium situation, the two excesses are linked by

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

Both equilibrium temperatures pertaining to the points B or C or nonequilibrium temperature $\tilde{T}$ at A are acceptable in Eq. (14) in the near-equilibrium case. In this case, any conventional variable ($\tilde{P}$, $\tilde{T}$, etc.) can be replaced by its equilibrium values (P, T, etc.) in the *multiplicative coefficients* of any relationship [consider, e.g., Eq. (22)].

III. NONEQUILIBRIUM ENERGY CORRECTION FROM THE KINETIC THEORY

It is essential to recognize that the entropy representation is natural for the formalism of the kinetic theory[6] in which, by definition, the internal energy comprises the only contribution except that of macroscopic motion $u^2/2$ 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 $T_{(C)}$ and $P_{(C)}$. From this formalism one determines the nonequilibrium corrections $\Delta\tilde{s}$ or $\Delta\tilde{e}$ in terms of the nonequilibrium density distribution function $\tilde{f}$. Here, for the reader's convenience, we recapitulate the results of several authors (Grad,[6] Lebon,[1] Jou and Casas Vazquez,[7,12] and others) for dilute gas of rigid spheres in the relaxation-time approximation of the Boltzmann equation. The molecular velocity distribution function $\tilde{f}$, out of equilibrium but close to it, is given in the form

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

where f is the local equilibrium (Maxwell-Boltzmann) distribution pertaining to the entropy representation equilibrium (point C, Fig. 1). $\tilde{f}$ and f 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 **q** in Grad's method. Using (15) in the definition of entropy, one integrates the expression $\tilde{f}\ln\tilde{f}$ over all of the space of the molecular velocity **c**,

$$\tilde{\rho}\tilde{s}=-k\int\tilde{f}\ln\tilde{f}\,d\mathbf{c}\ . \tag{16}$$

Proceeding with development of $\tilde{s}$ up to second order in ϕ_1, one obtains[3]

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

with local equilibrium entropy

$$\rho s=-k\int f\ln f\,d\mathbf{c} \tag{18}$$

and nonequilibrium correction

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

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

$$\rho e^{(1)}=\int\phi_1 fmc^2d\mathbf{c}\ , \tag{19b}$$

which corresponds to reaching the minimum energy if $\rho e^{(1)}=0$. The second-order correction to the entropy density (entropy representation) is

$$\rho s^{(2)}=\tilde{\rho}\Delta\tilde{s}=-\tfrac{1}{2}k\int f\phi_1^2d\mathbf{c}\ . \tag{20}$$

Hence

$$\Delta\tilde{e}=(kT/2)\rho\int f\phi_1^2d\mathbf{c}\ . \tag{21}$$

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 **q**, is[6,7]

$$\phi_1=\tfrac{2}{5}(m/Pk^2T^2)(1/2mC^2-5/2kT)\mathbf{C}\cdot\mathbf{q}\ , \tag{22}$$

where m is the mass of a molecule. From Eqs. (20), (21), and (22) one obtains for the entropy deviation

$$\Delta\tilde{s}=-(m/5\rho PkT^2)\mathbf{q}^2 \tag{23}$$

and for the energy deviation, Eq. (14), in terms of the entropy flux ($\mathbf{j}_s=\mathbf{q}T^{-1}$ to the accuracy of the thirteenth moment of the velocity[6]):

$$\Delta\tilde{e}=\tfrac{1}{5}(m^2/k^2\rho^2)\mathbf{j}_s^2=\tfrac{1}{2}\rho^{-2}g\,\mathbf{j}_s^2\ . \tag{24}$$

We have now abandoned the entropy representation. When passing from Eq. (23) to (24) the state equation $P=\rho kTm^{-1}$ is used and the constant g is defined as

$$g=2mT\rho/5Pk=2m^2/5k^2\ . \tag{25}$$

The pressure in Eqs. (22) and (25) is the ideal-gas pressure, given by the definition used in the kinetic theory.[6]

Equation (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 the generalized definition of g obtained by comparing Eqs. (4) and (24),

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

In the ideal-gas case the derivative $\partial^2\tilde{e}/\partial\mathbf{j}_s^2=\frac{2}{5}(m^2/k^2\rho^2)$ from Eq. (24) and the definition (25) is immediately recovered given the definition (26). Sieniutycz's[19] hypothesis about the equality of the kinetic and static nonequilibrium energy corrections in a thermal shock wave front can be used to compute $(\partial^2\tilde{e}/\partial\mathbf{j}_s^2)^{\text{eq}}$ for arbitrary fluids as $T/\rho c_p G$ and hence g as $T\rho/c_p G$ where G is the shear modulus. For the ideal gas, the shear modulus is just the pressure P (a result known by Maxwell) and $c_P=5k/2m$, which allows one to recover definition (25) from the expression $g=T\rho/c_P G$ and supports the hypothesis mentioned above. However, for the purpose of this paper, the use of the implicit dependence of g on the basic variables $(\tilde{\rho},\tilde{s})$ will be enough, i.e., the function $g(\tilde{\rho},\tilde{s})$ will be used when passing to arbitrary fluids. Equation (24) shows that if the coordinates $\tilde{s}$, $\tilde{\rho}$ (or $\tilde{v}$), and $\mathbf{j}_s$ are used, then (with accuracy to second-order terms) the nonequilibrium energy correction of an ideal gas does not depend explicitly on entropy $\tilde{s}$. Therefore, the nonequilibrium corrections $\Delta\tilde{T}$ and $\Delta\tilde{P}$ in the energy representation, Eqs. (8) and (9), are, respectively,

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

and

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

The entropy flux adjoints $\mathbf{a}_s$ and $\mathbf{j}_s$, Eq. (10), are, respectively,

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

and

$$\mathbf{i}_s=g\tilde{\rho}^{\,-1}\mathbf{j}_s=g\tilde{s}\mathbf{v}_s \ . \tag{29b}$$

The entropy diffusion velocity $\mathbf{v}_s\equiv\mathbf{j}_s/\tilde{\rho}\tilde{s}$ was introduced in Eq. (29b). One could also introduce there the product $kg\tilde{s}$, which has the dimension of mass. For the ideal gas this product is $m_s=\frac{2}{5}(m^2\tilde{s}k^{-1})$, which is a measure of heat inertia. Equations (27)–(29) can also be obtained from Eqs. (11)–(13). From Eqs. (6), (7), (27), and (28) one has for an ideal gas in energy representation

$$\tilde{T}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=T(\tilde{s},\tilde{\rho}) \tag{30}$$

and

$$\tilde{P}(\tilde{s},\tilde{\rho},\mathbf{j}_s)=P(\tilde{s},\tilde{\rho})-g\tilde{\rho}^{\,-1}\mathbf{j}_s^2 \tag{31}$$

in the sense of definitions (8) and (9). Note that $\tilde{e}\neq e$ in this representation (Fig. 1, points A and B).

The nonequilibrium temperatures and pressures were considered by Jou and Casas Vazquez[7] in the entropy representation. They defined nonequilibrium corrections to equilibrium quantities in terms of the partial derivatives of the function $\tilde{s}(\tilde{e},\tilde{\rho}^{\,-1},\mathbf{q})$ with respect to $\tilde{e}$ and $\tilde{\rho}^{\,-1}$ taken at constant $\mathbf{q}$ rather than constant $\mathbf{j}_s$. In this section of our work, "nonequilibrium" $\tilde{T}$ and $\tilde{P}$ are defined in terms of the partial derivatives of the nonequilibrium energy $\tilde{e}(\tilde{s},\tilde{\rho}^{\,-1},\mathbf{j}_s)$ with respect to $\tilde{s}$ and $\tilde{\rho}$ (or $\tilde{\rho}^{\,-1}=\tilde{v}$) taken at constant $\mathbf{j}_s$. Furthermore, the reference (equilibrium) states are not equivalent in the two representations. When this distinction is kept in mind the two results become consistent, although in either case there is no guarantee that $\mathbf{q}$ or $\mathbf{j}_s$ are natural variables of the Gibbs's equation; see Sec. VIII for an explanation of this important point. As Eq. (30) indicates, $\tilde{T}$ of Eq. (30) is equal to the equilibrium temperature $T(\tilde{\rho},\tilde{s})$, 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 $\mathbf{j}_s$, not the heat flux $\mathbf{q}$, as the nonequilibrium variable in energy function $\tilde{e}$. If one differentiates the nonequilibrium entropy $\tilde{s}$ with respect to the energy holding $\mathbf{q}$ constant, then one obtains the reciprocal of the nonequilibrium temperature of Jou and Casas Vazques[7] $\tilde{T}_{(C)}$, which differs from the reciprocal of the corresponding equilibrium temperature T by a term quadratic in $\mathbf{q}$. In general, the nonequilibrium temperatures are not the measures of mean kinetic energy (understood as the fifth moment of the both nonequilibrium and equilibrium density functions[20]). The nonequilibrium temperatures and pressures discussed in this section and Sec. IV 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., Eq. (9)] computed for definite variables. The same pertains to the corrections $\Delta\tilde{T}$ and $\Delta\tilde{P}$. They are generated here for the purpose of collecting definite partial derivatives to be used in variational computations, but the question of the proper (natural) set of nonequilibrium variables in $\tilde{e}$ is still open. We return to this question in Sec. VIII.

In what follows, we will always describe the nonequilibrium states in terms of the equilibrium quantities of definite representation and nonequilibrium fluxes ($\mathbf{j}_s$, or $\mathbf{q}$). Such a description is representation dependent and thus needs careful handling; however, it allows one to exploit the well-known functions of the classical equilibrium thermodynamics.

IV. NONEQUILIBRIUM ENERGY EQUATIONS AND THE KINETIC POTENTIAL

We are now prepared to obtain the two basic quantities that will be used to characterize the moving nonequilibrium gas, the total volumetric energy $\tilde{E}$, and the corresponding kinetic potential L, and to give the explicit formulas for the perfect derivatives of these quantities. Next, the formulas will be exploited to accomplish the main goal of this paper, determining the components of the energy-momentum tensor and the corresponding conservation laws for the system considered.

If our nonequilibrium fluid moves with the hydrodynamic velocity $\mathbf{u}$ (mass flux $\mathbf{J}=\tilde{\rho}\mathbf{u}$) in the weak external scalar field $\psi(\mathbf{x},t)$, the total volumetric energy $\tilde{E}$ of the fluid is, in the energy representation,

$$\tilde{E}=\tilde{\rho}e(\tilde{s},\tilde{\rho})+\tfrac{1}{2}\tilde{\rho}^{-1}g\,\mathbf{j}_s^2+\tfrac{1}{2}\tilde{\rho}^{-1}\mathbf{J}^2+\tilde{\rho}\psi(x,t)\ . \tag{32}$$

The first two terms on the right describe, respectively, the densities of the internal energy at equilibrium and the nonequilibrium component of the internal energy. The last two terms express, respectively, the density of the kinetic energy and potential energy. In the entropy representation the total energy (32) becomes (Fig. 1)

$$\tilde{E}=\tilde{\rho}\,\tilde{e}+\tfrac{1}{2}\tilde{\rho}^{-1}\mathbf{J}^2+\tilde{\rho}\psi(\mathbf{x},t)\ , \tag{33}$$

which is just the usual energy formula used in the nonequilibrium thermodynamics and kinetic theory. Comparison of two representations reveals an effect of appearance or disappearance of various kinetic terms when passing from one to another representation. Further, only the energy representation is used for the purpose of construction of Hamilton's principle. The perfect differential of $\tilde{E}$, Eq. (32) has the form

$$\begin{aligned}\tilde{d}\tilde{E}=\tilde{\rho}Td\tilde{s}+(P\tilde{\rho}^{-1}+e-\tfrac{1}{2}g\tilde{\rho}^{-2}\mathbf{j}_s^2-\tfrac{1}{2}\mathbf{u}^2+\psi)d\tilde{\rho}\\ +\tilde{\rho}^{-1}g\,\mathbf{j}_s\cdot d\,\mathbf{j}_s+\mathbf{u}\cdot d\mathbf{J}-\tilde{\rho}\mathbf{F}\cdot d\mathbf{x}+\tilde{\rho}\psi_t dt\ ,\end{aligned} \tag{34}$$

where $\mathbf{u}=\mathbf{J}\tilde{\rho}$, $\mathbf{F}=-\nabla\psi$ (the external force), and $\psi_t=\partial\psi/\partial t$. Equation (34) has a somewhat unusual form because the variables typical of the Eulerian fluid theory (with the extra variable $\mathbf{j}_s$) are used to express the total differential of the volumetric energy. When the more popular variables $\tilde{\rho}\tilde{s},\tilde{\rho},\mathbf{u}=\mathbf{J}/\tilde{\rho}$ are used and the velocity of the entropy diffusion $\mathbf{v}_s=\mathbf{j}_s/\tilde{\rho}\tilde{s}$ is introduced, then Eq. (34) takes the more conventional form

$$\begin{aligned}d\tilde{E}=(T+g\tilde{s}\mathbf{v}_s^2)d(\tilde{\rho}\tilde{s})+(\mu+\psi+\mathbf{u}^2/2+g\tilde{\rho}\mathbf{v}_s^2)d\tilde{\rho}\\ +g\tilde{s}\,\mathbf{j}_s\cdot d\,\mathbf{v}_s+\mathbf{J}\cdot d\,\mathbf{u}-\tilde{\rho}\mathbf{F}\cdot d\,\mathbf{x}+\tilde{\rho}\psi_t dt\ ,\end{aligned} \tag{35}$$

where $\mu=(\partial\rho e/\partial\rho)_{\rho s}$ is the equilibrium chemical potential. Finally, the perfect differential of the specific total energy $\tilde{e}=\tilde{E}/\tilde{\rho}$, the counterpart of (5), is

$$\begin{aligned}d(\tilde{E}/\tilde{\rho})=Td\tilde{s}-(P-g\tilde{V}\mathbf{j}_s^2)d\tilde{V}+g\tilde{V}\tilde{s}\mathbf{v}_s\cdot d\,\mathbf{j}_s\\ +\mathbf{u}\cdot d\,\mathbf{u}-\mathbf{F}\cdot d\,\mathbf{x}+\psi_t dt\ ,\end{aligned} \tag{36}$$

which agrees with Eqs. (29)–(31). We purposely have given the several equivalent energy equations (34)–(36) because it is instructive to observe how the typical energy derivatives ($\partial\tilde{E}/\partial\tilde{s}$, $\partial\tilde{E}/\partial\tilde{\rho}$, etc.) depend on the irreversible flux $\mathbf{j}_s$ in the system. We have indicated the care required to specify what is held constant in taking derivatives of $\tilde{E}$ and how the choice affects what one may use as a nonequilibrium temperature. But surely the *physics* must dictate which derivative should be used in any particular case, not the niceties of the form. Because of this sensitivity, we operate with isoentropic equilibrium temperature $T(\tilde{\rho},\tilde{s})$ and pressure $P(\tilde{\rho},\tilde{s})$ and the definite corrections (for definite variables used) as the functions of $\mathbf{v}_s^2$ or $\mathbf{j}_s^2$ and do not yet use any nonequilibrium temperatures or pressures. However, we will return to the question of the definition of $\tilde{T}$ and $\tilde{P}$ in Sec. VIII.

The most fundamental quantity from the viewpoint of purposes of this work is not energy density $\tilde{E}$ but the so-called kinetic potential L. 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 ($\tilde{\rho}\mathbf{u}=\mathbf{J}$ 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. (33), the situation is more involved because the energy may change not only by the motion of mass (the $\mathbf{J}$ flux) but also by the motion of entropy (the $\mathbf{j}_s$ flux). Consequently, one has to decide whether to use the conventional Legendre transform with $\mathbf{J}$ only, or to choose an extended (double) Legendre transform, using both $\mathbf{J}$ and $\mathbf{j}_s$ or $\mathbf{J}$ and $\mathbf{i}_s$, etc. These two are

$$L^0=(\partial\tilde{E}/\partial\mathbf{J})\cdot\mathbf{J}-\tilde{E}(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{j}_s)\ , \tag{37}$$

$$\begin{aligned}L&=(\partial\tilde{E}/\partial\mathbf{J})\cdot\mathbf{J}+(\partial\tilde{E}/\partial\mathbf{j})_s\cdot\mathbf{j}_s-\tilde{E}(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{j}_s)\\ &=(\partial\tilde{E}/\partial\mathbf{J})\cdot\mathbf{J}+(\partial\tilde{E}/\partial\mathbf{a}_s)\cdot\mathbf{a}_s-\tilde{E}(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{j}_s)\\ &=(\partial\tilde{E}/\partial\mathbf{J})\cdot\mathbf{J}+(\partial\tilde{E}/\partial\mathbf{i}_s)\cdot\mathbf{i}_s-\tilde{E}(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{i}_s)\ .\end{aligned} \tag{38}$$

Due to the linearity of relationship linking $\mathbf{j}_s$, $\mathbf{a}_s$, and $\mathbf{i}_s$, the three forms of Eq. (38) yield the same result, Eq. (41). The unambiguous answer is the latter, L, Eq. (38), as will be shown in the following sections. The introduction of the entropy flow terms into (38) is of course an ansatz. However, we will show that only the extended kinetic potential, Eq. (38), allows one to recover the proper energy formula, Eq. (32), from the approach through Hamilton's principle. Furthermore, Eq. (38) suggests how to generalize L if any other independent, nonequilibrium variable is introduced, in addition to or instead of $\mathbf{j}_s$; for instance, electric current $\mathbf{j}_e$ and mass diffusion fluxes $\mathbf{j}_i$ ($i=1,2,\ldots,n$) in the multicomponent case.

V. THE APPROACH THROUGH HAMILTON'S PRINCIPLE

After the Legendre transformation is performed one may express the kinetic potential L so obtained in terms of arbitrary variables, i.e., the use of velocities is not necessary and fluxes $\mathbf{J}$ and $\mathbf{j}_s$ still can be used. The basic role of the kinetic potential is in its use in Hamilton's principle, where, by Noether's theorem, all components of the energy-momentum tensor G^{jk} are obtained and the energy $\tilde{E}$ is recovered in its correct form, Eq. (32), as the component G^{44} of the G^{jk}. The procedure is illustrated by the following scheme in which the question marks designate the originally unknown quantities:

$$\begin{bmatrix} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & \tilde{E} \end{bmatrix} \xrightarrow{\text{Legendre transformation}} L \xrightarrow{\text{Hamilton's principle and Noether's theorem}} \begin{bmatrix} T^{11} & T^{12} & T^{13} & \Gamma^{1} \\ T^{21} & T^{22} & T^{23} & \Gamma^{2} \\ T^{31} & T^{32} & T^{33} & \Gamma^{3} \\ \Omega^{1} & \Omega^{2} & \Omega^{3} & \tilde{E} \end{bmatrix}, \tag{39}$$

where the kinetic potential L can be obtained from either Eq. (37) or Eq. (38). The energy-momentum tensor that is sought contains four kinds of quantities. One is the purely spatial part $T^{\alpha\beta}$ which is the stress tensor (the negative of $T^{\alpha\beta}$ is the pressure tensor). Second are the terms $G^{\alpha 4}=\Gamma^{\alpha}$, the components of the momentum density vector ($\mathbf{J}=\tilde{\rho}\mathbf{u}$ in the classical case), and the third Ω^{β}, the components of the energy flux vector. When a proper Legendre transformation is used we expect to recover, as the component G^{44}, the same energy $\tilde{E}$ as that with which we started. Therefore, the roles of the complex energy formulas and complex energy equations such as Eqs. (32) and (34) lie, *inter alia*, in their provision of all the components of energy-momentum tensor according to the scheme (39); using this tensor, we can write down the balance equations for energy and momentum. With the energy given by (32), the two Legendre transformations (37) and (38) yield

$$L^{0}=\tfrac{1}{2}\tilde{\rho}^{-1}\mathbf{J}^{2}-\tfrac{1}{2}\tilde{\rho}^{-1}g\,\mathbf{j}_{s}^{2}-\tilde{\rho}e(\tilde{\rho},\tilde{s})-\tilde{\rho}\psi(\mathbf{x},t) \tag{40}$$

and

$$L=\tfrac{1}{2}\tilde{\rho}^{-1}\mathbf{J}^{2}+\tfrac{1}{2}\tilde{\rho}^{-1}g\,\mathbf{j}_{s}^{2}-\tilde{\rho}e(\tilde{\rho},\tilde{s})-\tilde{\rho}\psi(\mathbf{x},t)\ , \tag{41}$$

differing only in the sign of the second term.

According to Hamilton's principle, the four-dimensional integral of L taken over the space-time must be stationary under the constraints resulting from the entropy and mass balances and reversibility of the process. The last condition is restrictive in the sense that it cannot allow one to obtain the kinetic equations linking thermodynamic fluxes and forces when irreversible terms are present. Only truncated forms of these equations (without irreversible, time-unsymmetrical terms) can be obtained. One should then additionally exploit the second law of thermodynamics in order to determine the class of irreversible terms which are not excluded by this law. Since, however, the balance equations for energy and momentum are the same for reversible and irreversible behavior, one can use Hamilton's principle to determine the proper form of the conservation laws, the task of the present work for the fluid with heat flow. Such conservation laws, expressed in terms of the four-divergences of the energy-momentum tensor (constructed from the kinetic potential L), serve for both reversible and irreversible processes.

The notion of the thermodynamic reversibility assumed in this work should be explained. Of course, it corresponds to entropy conservation, i.e., to vanishing entropy production $\sigma=\tilde{\lambda}^{-1}\mathbf{j}_{s}^{2}$ where $\tilde{\lambda}$ is the heat conductivity. (The entropy production expression for heat flux is in the form which is identical in classical and extended thermodynamics.) However, the vanishing of σ can be attained in two limiting cases, through vanishing diffusive flux ($\mathbf{j}_{s}=\mathbf{0}$ or $\mathbf{q}=\mathbf{0}$) or through infinite heat conductivity, i.e., taking $\tilde{\lambda}\rightarrow\infty$. The first case is that of the Eulerian fluid for which, by assumption, no heat exchange occurs between the individual fluid particles, so that $\mathbf{j}_{s}=\mathbf{q}=\mathbf{0}$ even if ΔT is finite. (This corresponds to vanishing of both heat flow and heat conductivity, with $\mathbf{j}_{s}^{2}$ tending to zero faster than $\tilde{\lambda}$, allowing σ to go to zero.) This case is of no interest to us since it removes the heat and entropy fluxes, truncates our equations, and eliminates the entropy effects which are just what concern us. Therefore, we are interested in the second limiting case of reversibility, i.e., reversibility approached by excellent heat conductivity, a "heat superconductor." It is similar to that occurring in so-called collisionless plasmas where ideal motion of electric charges can occur. An example of a heat superconductor would be liquid helium or any fluid or crystal with purely harmonic interactions between neighboring molecules. However, it should be remembered that this reversibility is no more than just a theoretical limit at which we can derive exact conservation laws from Hamilton's principle. Any real system for which we want to apply our tensor G^{jk} need not necessarily be reversible, but only conform to the energy equations (32) or (34).

If in Eq. (32) the constant g, Eq. (25), is used, then the case considered would pertain to the kinetic theory of the nonequilibrium dilute ideal gas. One may wish to consider the effects caused by its generalization to the form (26) when g depends on $\tilde{\rho}$ and $\tilde{s}$ since such a form is appropriate for real gases and fluids. It turns out that the ideal gas case is quite special and many substantial properties of the method used and the system considered are lost or masked if one restricts oneself to the case of constant g. Therefore, the general case of an arbitrary function $g(\tilde{s},\tilde{\rho})$ will be analyzed below.

Hamilton's principle in the Eulerian (field) representation of the fluid motion is used here. The constraints resulting form the conservation of mass and entropy are taken into account by using the method of Lagrange multipliers. Hence the following expressions,

$$\beta(\mathbf{x},t)(\partial\tilde{\rho}/\partial t+\nabla\cdot\mathbf{J})=0\ , \tag{42}$$

$$\eta(\mathbf{x},t)[\partial\tilde{\rho}\tilde{s}/\partial t+\nabla\cdot(\mathbf{J}\tilde{s}+\mathbf{j}_{s})]=0\ , \tag{43}$$

are added to the kinetic potential L in the action integral. Here β and η are the field functions describing the Lagrangian multipliers associated with the mass and entropy conservation. The sum $\mathbf{J}\tilde{s}+\mathbf{j}_{s}$ in Eq. (43) is the total entropy flux composed of the convective part $\mathbf{J}\tilde{s}=\tilde{\rho}\mathbf{u}\tilde{s}$ and the diffusive part $\mathbf{j}_{s}$. As is well known, the diffusive part $\mathbf{j}_{s}$ is related to heat flux, but we make no assumption about the outcomes of our search for an energy-momentum tensor G^{jk}. Thus, in this approach, the entropy flux is a more fundamental quantity than the heat flux $\mathbf{q}$. The relativistic invariance of the 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 our approach.

In addition to the constraints associated with Eqs. (42) and (43) one more constraint should be taken into account. This is the so-called Lin constraint[2] preserving the identity of each definite fluid particle. It results in the constancy of the Lagrangian coordinate $\alpha(\mathbf{x},t)$ of this particle ($d\alpha/dt=0$) along the path. Scalar α can be used in the case of our displacement-free model.[5] Hence the expression

$$\lambda(\mathbf{x},t)(\tilde{\rho}\partial\alpha/\partial t+\mathbf{J}\cdot\nabla\alpha)=0\ , \tag{44}$$

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

$$\begin{aligned}A'=\int\int\int\int\{&L(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{j}_s,\mathbf{x},t)+\beta(\partial\tilde{\rho}/\partial t+\nabla\cdot\mathbf{J})\\&+\eta[\partial\tilde{\rho}\tilde{s}/\partial t+\nabla\cdot(\mathbf{j}J\tilde{s}+\mathbf{j}_s)]\\&+\lambda(\tilde{\rho}\partial\alpha/\partial t+\mathbf{J}\cdot\nabla\alpha)\}dV\,dt\ ,\end{aligned} \tag{45}$$

which, however, leads to components of the energy-momentum tensor G^{jk} containing the Lagrangian multipliers explicitly. In order to make A' and the corresponding G^{jk} physical (without the multipliers) the expressions (42) and (43) in Eq. (45) are transformed, in the known way, by using the divergence theorem and rejecting four-divergences obtained.[21] This procedure does not affect the stationary conditions of the action and yields

$$\begin{aligned}A&=\int\int\int\int\Lambda dV\,dt\\&=\int\int\int\int\{L(\tilde{\rho},\tilde{s},\mathbf{J},\mathbf{j}_s,\mathbf{x},t)-(\tilde{\rho}\partial\beta/\partial t+\mathbf{J}\cdot\nabla\beta)\\&\qquad-[\tilde{\rho}\tilde{s}\partial\eta/\partial t+(\mathbf{J}\tilde{s}+\mathbf{j}_s)\cdot\nabla\eta]\\&\qquad+\lambda(\tilde{\rho}\partial\alpha/\partial t+\mathbf{J}\cdot\nabla\alpha)\}dV\,dt\ .\end{aligned} \tag{46}$$

In the case in which $\mathbf{j}_s=\mathbf{0}$ in L and in the η term of Eq. (46), our functional goes over into the Eulerian fluid functional, which is the basic quantity serving to construct the variational theory of this fluid. Many results have been obtained in this case, but we will not discuss them here, referring the reader to Refs. 8, 13, and 14, and, in particular, to the review[8] where many further references can be found. It can be shown that the physical meeting of the Lagrangian multipliers remains the same as in the case of the Eulerian fluid,[13,14,21] namely, β is the velocity potential when the flow is irrotational and at the same time the Lagrangian action of a fluid particle that has the initial velocity λ. The convective derivative of η is just a nonequilibrium temperature $\tilde{T}$ [compare Eqs. (50), (54), and (77)].

VI. STATIONARITY CONDITIONS OF THE ACTION

The Euler equations of the functional (46) with respect to the field variables β,η allow one to recover conservation laws for mass, entropy, and identity of fluid particles. The stationarity conditions of A with respect to the variables $\mathbf{J}$, $\tilde{\rho}$, $\mathbf{j}_s$, and $\tilde{s}$ are

$$\text{for } \partial\mathbf{J}:\quad \partial L/\partial\mathbf{J}-\nabla\beta-\tilde{s}\nabla\eta+\lambda\nabla\alpha=\mathbf{0}, \tag{47}$$

$$\text{for } \partial\rho:\quad \partial L/\partial\tilde{\rho}-\partial\beta/\partial t-\tilde{s}\partial\eta/\partial t+\lambda\partial\alpha/\partial t=0\ , \tag{48}$$

$$\text{for } \partial\mathbf{j}_s:\quad \partial L/\partial\mathbf{j}_s-\nabla\eta=\mathbf{0}\ , \tag{49}$$

$$\text{for } \partial\tilde{s}:\quad \partial L/\partial\tilde{s}-\tilde{\rho}\partial\eta/\partial t-\mathbf{J}\cdot\nabla\eta=0\ . \tag{50}$$

These equations are valid for any arbitrary function $L(\mathbf{J},\tilde{\rho},\mathbf{j}_s,\tilde{s})$. For the two kinetic potentials L we want to compare, Eqs. (40) and (41), the derivatives $\partial L/\partial\mathbf{J}$, $\partial L/\partial\tilde{s}$, etc., are

$$\partial L/\partial\mathbf{J}=\tilde{\rho}^{-1}\mathbf{J}=\mathbf{u}\ , \tag{51}$$

$$\partial L/\partial\tilde{\rho}=-[h+\mathbf{u}^2/2+\psi\mp\tfrac{1}{2}g\tilde{s}^{\,2}\mathbf{v}_s^2\pm\tfrac{1}{2}(\partial g/\partial\rho)_s\rho^{-1}\mathbf{j}_s^2]\ , \tag{52}$$

$$\partial L/\partial\mathbf{j}_s=\mp g\tilde{s}\mathbf{v}_s\ , \tag{53}$$

$$\partial L/\tilde{\rho}\partial\tilde{s}=-[T(\tilde{\rho},\tilde{s})\pm\tfrac{1}{2}\tilde{\rho}^{-2}(\partial g/\partial\tilde{s})_\rho\mathbf{j}_s^2]\ . \tag{54}$$

In the above equations and the following text, upper signs always pertain to L of Eq. (40), and lower signs to L of Eq. (41).

VII. APPLICATION OF THE NOETHER THEOREM

The conservation laws and the components of the energy-momentum tensor can be obtained either by transforming the stationary conditions or from the Noether theorem. The second method, although more formal than the first one, is, as a rule, easier than the first and is especially recommended if the construction of conservation laws is the primary goal and stationarity conditions are of less interest. Since this is the case here, we will use the formula for the energy-momentum tensor G^{jk} resulting from the first Noether theorem. It gives the conditions for invariance of the action A with respect to the translations in space and time in the form of the vanishing four-divergence of the tensor G^{jk} and defines the structure of this tensor, Eq. (56). For the general action functional

$$A(\mathbf{a}(\tilde{\mathbf{x}}))=\int\int\int\int\Lambda(\mathbf{a}(\tilde{\mathbf{x}}),\partial\mathbf{a}/\partial\tilde{\mathbf{x}},\tilde{x})dV\,dt\ , \tag{55}$$

where $\mathbf{a}=(a_1,a_2,\ldots,a_l,\ldots,a_s)$ is the vector of field variables and $\tilde{\mathbf{x}}=(x_1,x_2,x_3,t)$ is the enlarged vector of the independent variables, i.e., space-time coordinates, the Noether theorem yields the following expression for G^{jk} (c.f., Refs. 10 and 11):

$$G^{jk}=\sum_l(\partial a_l/\partial\tilde{x}^{\,j})[\partial\Lambda/\partial(\partial a_l/\partial\tilde{x}^{\,k})]-\delta^{jk}\Lambda\ . \tag{56}$$

The four-divergence of the above quantity should vanish identically in the case of absence of external fields (i.e., when Λ does not contain $\mathbf{x}$ and t explicitly). This means that the conservation laws hold for G^{jk}.

The presence of external fields, such as, e.g., our scalar field $\psi(\mathbf{x},t)$, results in the explicit dependence of Λ on $\tilde{\mathbf{x}}$, and then the condition of the vanishing four-divergence of G^{jk} should be replaced by the relationship

$$\sum_k (\partial G^{jk}/\partial \tilde{x}^k)+\partial\Lambda/\partial\tilde{x}^j=0 \quad (j,k=1,2,3,4) , \tag{57}$$

which constitutes the concise formulation of balance equations for the momentum ($j=1,2,3$) and the energy ($j=4$). For an arbitrary Lagrangian the tensor G^{jk}, Eq. (56) is, in general, unsymmetrical. The physical considerations which can be found, e.g., in field theory[11] or variational calculus,[10] show that the G^{jk} should be symmetric at least with respect to this spatial part if micropolar effects are excluded (the case considered here). In relativistic theories the symmetry of the whole tensor G^{jk} is required.[11] We will show that the structure of the Lagrangian Λ in Eq. (46) is physical in the sense that it leads to the G^{jk} tensor without Lagrangian multipliers and that the spatial part of G^{jk}, i.e., the stress tensor $T^{\alpha\beta}$, is symmetric.

From the general equations (58) and (59) the components of G^j_k tensor are now evaluated. For the action A, Eq. (46), the following partial derivatives are computed:

$$\partial\Lambda/\partial(\partial\beta/\partial t)=-\tilde{\rho} , \tag{58}$$

$$\partial\Lambda/\partial(\nabla\beta)=-\mathbf{J} , \tag{59}$$

$$\partial\Lambda/\partial(\partial\eta/\partial t)=-\tilde{\rho}\tilde{s} , \tag{60}$$

$$\partial\Lambda/\partial(\nabla\eta)=-(\mathbf{J}\tilde{s}+\mathbf{j}_s) , \tag{61}$$

$$\partial\Lambda/\partial(\partial\alpha/\partial t)=\tilde{\rho}\lambda , \tag{62}$$

$$\partial\Lambda/\partial(\nabla\alpha)=\mathbf{J}\lambda . \tag{63}$$

Equations (58)–(63) are independent of the form of the kinetic potential L. Next, the general equation (56) is used. For the stress tensor one obtains ($\alpha,\beta=1,2,3$)

$$\begin{aligned} G^\alpha{}_\beta=T^\alpha{}_\beta=&-(\partial\beta/\partial x^\alpha)J_\beta-(\partial\eta/\partial x^\alpha)(J_\beta\tilde{s}+j_{s\beta})\\ &+(\partial\alpha/\partial x^\alpha)J_\beta\lambda-\Lambda\delta^\alpha_\beta . \end{aligned} \tag{64}$$

To evaluate the stationary Λ appearing in Eq. (64) the stationarity conditions (47)–(50) are used in the integrand of Eq. (46). For arbitrary $L(\tilde{\rho},\mathbf{J},\mathbf{j}_s,\tilde{s},\mathbf{x})$ we obtain the Lagrangian

$$\Lambda=L-\tilde{\rho}(\partial L/\partial\tilde{\rho})-\mathbf{J}\cdot(\partial L/\partial\mathbf{J})-\mathbf{j}_s\cdot(\partial L/\partial\mathbf{j}_s) . \tag{65}$$

With the kinetic potentials (40) and (41) associated with the classical and extended Legendre transforms, Eqs. (65) and (51)–(53) yield

$$\begin{aligned} \Lambda=&\tfrac{1}{2}\rho^{-1}\mathbf{J}^2\mp\tfrac{1}{2}\tilde{\rho}^{-1}g\,\mathbf{j}_s^2-\tilde{\rho}(e+\psi)+\tilde{\rho}h+\tfrac{1}{2}\tilde{\rho}^{-1}\mathbf{J}^2\\ &+\tilde{\rho}\psi\mp\tfrac{1}{2}\tilde{\rho}g\tilde{s}^2V_s^2\pm\tfrac{1}{2}(\partial g/\partial\tilde{\rho})_{\tilde{s}}\mathbf{j}_s^2\\ &-\tilde{\rho}^{-1}\mathbf{J}^2\pm\tilde{\rho}g\tilde{s}^2V_s^2 , \end{aligned} \tag{66}$$

where the upper signs pertain to Eq. (40) and lower signs to Eq. (41). Since $h=e+\tilde{\rho}^{-1}P$, Eq. (66) yields

$$\hat{\Lambda}=P(\tilde{\rho},\tilde{s})\pm\tfrac{1}{2}(\partial g/\partial\tilde{\rho})_{\tilde{s}}\mathbf{j}_s^2 . \tag{67}$$

Contrary to the corrections such as in Eq. (28) which depend on the variable used ($\mathbf{j}_s$, $\mathbf{q}$, $\mathbf{a}_s$, etc.), when differentiating $\tilde{e}$ with respect to $\tilde{\rho}$ (or $\tilde{v}$) the expression (67) is invariant with respect to change of variables—the result of the invariance of the variational problems. This suggests that the stationarity Lagrangian is equal to a nonequilibrium pressure. Later we will show that the lower sign result is indeed the nonequilibrium pressure at point A, Fig. 1, obtained when differentiating the nonequilibrium energy $\tilde{e}$ versus $\tilde{v}$ and keeping constant the entropy $\tilde{s}$ and the thermal momentum $\mathbf{i}_s$ (the "natural" variables of $\tilde{e}$). Equation (67) is a generalization of the result known for the equilibrium Eulerian fluid without heat in both Newtonian[5] and relativistic[13,14] cases where $\Lambda=P$. So far it is impossible to conclude which kinetic potential, Eq. (40) or Eq. (41), is the proper one. Using stationarity conditions (47)–(49), derivative expressions (51)–(53) and Eq. (67) in Eq. (64) yields the stationary stress tensor $T^{\alpha\beta}$ in the form ($\alpha,\beta=1,2,3$)

$$\begin{aligned} G^\alpha{}_\beta=T^\alpha{}_\beta=&-(\partial L/\partial J^\alpha)J_\beta-(\partial L/\partial j_s^\alpha)j_{s\beta}-\Lambda\delta^\alpha_\beta\\ =&-\tilde{\rho}u^\alpha u_\beta\pm\tilde{\rho}g\tilde{s}^2V_s^\alpha V_{s\beta}\\ &-[P(\tilde{\rho},\tilde{s})\pm\tfrac{1}{2}(\partial g/\partial\tilde{\rho})_s j_s^2]\delta^\alpha_\beta . \end{aligned} \tag{68}$$

Equations (40) and (41) lead also to the same vector of the momentum density $G^\alpha{}_4=\Gamma^\alpha$ for which one obtains ($\alpha=1,2,3$)

$$\begin{aligned} -G^\alpha{}_4=-\Gamma^\alpha=&(\partial\beta/\partial x^\alpha)\tilde{\rho}+(\partial\eta/\partial x^\alpha)\tilde{\rho}\tilde{s}-(\partial\alpha/\partial x^\alpha)\tilde{\rho}\lambda\\ =&(\partial L/\partial J^\alpha)\tilde{\rho}=\tilde{\rho}u^\alpha . \end{aligned} \tag{69}$$

Thus momentum density is equal, as usual, to the mass flux $\mathbf{J}$. In energy representation, the equation of momentum balance resulting from the general formula, Eq. (57) taken for $j=1,2,3$, $k=1,2,3,4$ and Eqs. (68) and (69), is, in vector notation,

$$\begin{aligned} \partial\tilde{\rho}\mathbf{u}/\partial t=\nabla\cdot\{&\tilde{\rho}\mathbf{u}\mathbf{u}+\underline{1}[P\pm\tfrac{1}{2}(\partial g/\partial\tilde{\rho})\mathbf{j}_s^2]\\ &\mp g\tilde{\rho}\tilde{s}^2\mathbf{v}_s\mathbf{v}_s\}-\tilde{\rho}\mathbf{F}(\mathbf{x},t)=\mathbf{0} . \end{aligned} \tag{70}$$

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 ($\mathbf{J}=\mathbf{0}$). This effect is also predicted by Grad's[6] analysis of the Boltzmann equation.

Consider now the vector of the density of energy flux $\Omega_\beta=G^4{}_\beta$. Equation (56) and stationarity conditions (47)–(50) yield

$$\begin{aligned} G^4{}_\beta=\Omega_\beta=&-(\partial\beta/\partial t)J_\beta-(\partial\eta/\partial t)(J_\beta\tilde{s}+j_{s\beta})\\ &+(\partial\alpha/\partial t)J_\beta\lambda\\ =&-(\partial L/\partial\tilde{\rho})J_\beta\\ &-[\partial L/\tilde{\rho}\partial s-(\mathbf{J}/\tilde{\rho})\cdot(\partial L/\partial\mathbf{j}_s)]j_{s\beta} . \end{aligned} \tag{71}$$

Hence, for the kinetic potentials (40) and (41), one finds on the basis of Eqs. (51)–(54),

$$\begin{aligned} \Omega_\beta=\tilde{\rho}u_\beta[&\tfrac{1}{2}u^2+\psi+h\mp\tfrac{1}{2}g\tilde{s}^2V_s^2\pm\tfrac{1}{2}(\partial g/\partial\rho)_s\tilde{\rho}^{-1}j_s^2]\\ &\mp g\tilde{s}(\mathbf{u}\cdot\mathbf{v}_s)j_{s\beta}+[T\pm\tfrac{1}{2}\tilde{\rho}^{-2}(\partial g/\partial\tilde{s})_\rho j_s^2]j_{s\beta} . \end{aligned} \tag{72}$$

Equations (67), (70), and (72) show explicitly the effect caused by the form of the kinetic potential (40) (upper sign) and (41) (lower sign). To settle which formula is the correct one, we compute the total energy density $G^4{}_4=E$, Eq. (56), for $j=k=4$, which is

$$G^4{}_4=\tilde{E}=-(\partial\beta/\partial t)\tilde{\rho}-(\partial\eta/\partial t)\tilde{\rho}_s+(\partial\alpha/\partial t)\tilde{\rho}\lambda-\hat{\Lambda}$$
$$=-\tilde{\rho}(\partial L/\partial\tilde{\rho})-[P\pm\tfrac{1}{2}(\partial g/\partial\tilde{\rho})_s j_s^2] \;. \qquad (73)$$

When Eq. (52) is applied in (73), the result is

$$\tilde{E}=\tilde{\rho}[e(\tilde{\rho},\tilde{s})+u^2/2+\psi\mp\tfrac{1}{2}g\tilde{s}^{\,2}V_s^2] \;. \qquad (74)$$

Thus the true nonequilibrium energy density $\tilde{E}$, Eq. (33), is recovered only if we use the extended Legendre transformation, Eq. (38), and the nonclassical kinetic potential, Eq. (41). This result is of physical importance because it proves that in extending Hamilton's principle to nonequilibrium heat-flow phenomena, the entropy flux $\mathbf{j}_s$ or its adjoints $\mathbf{a}_s$ or $\mathbf{i}_s$ behave as they would if they were to play the role of a generalized momentum density, which must be taken into account together with the usual momentum density $\mathbf{J}$. The role of the classical transformation, Eq. (37), and corresponding kinetic potential, Eq. (40), is in fact finished now, since we have proven that only Eqs. (38) and (41) are correct. Therefore, in Eqs. (66)–(68), (70), (72), and (74) only the lower signs pertain to the true physical situations. Among the variables $\mathbf{q}$, $\mathbf{j}_s$, $\mathbf{a}_s$, or $\mathbf{i}_s$, the last one is crucial in Legendre transformation (38) due to its role in the nonequilibrium Gibbs equation (Sec. VIII).

At this point, one can easily write down the energy balance equation resulting from Eq. (57) for $j=4$, and Eqs. (72) and (74) taken with lower sign for $\beta=1,2,3$. In vector notation this balance reads

$$\begin{aligned}&\partial\tilde{\rho}(e+\tfrac{1}{2}u^2+\psi+\tfrac{1}{2}g\tilde{s}^{\,2}V_s^2)/\partial t\\&\quad+\nabla\cdot\{\tilde{\rho}\mathbf{u}[h+\tfrac{1}{2}u^2+\psi+\tfrac{1}{2}g\tilde{s}^{\,2}V_s^2-\tfrac{1}{2}(\partial g/\partial\rho)_s\tilde{\rho}^{\,-1}j_s^2]\\&\qquad+[T-\tfrac{1}{2}\tilde{\rho}^{\,-2}(\partial g/\partial s)_\rho j_s^2]\mathbf{j}_s\\&\qquad+(g\tilde{\rho}^{\,-1}\mathbf{j}_s\mathbf{j}_s)\cdot\mathbf{u}\}-\tilde{\rho}(\partial\psi/\partial t)=\mathbf{0} \;. \qquad (75)\end{aligned}$$

The last term in Eq. (75) is a source term analogous to the force term in Eq. (70). The energy can be conserved only when the external field is stationary ($\partial\psi/\partial t=0$). When the fluid is out of equilibrium, due to a nonvanishing heat flux, this energy contains, in the energy representation, the extra term $\tfrac{1}{2}g\tilde{s}^{\,2}V_s^2$, which appears also in the expression for energy flux. Heat flux appears naturally in the theory as the product of a nonequilibrium temperature and entropy flux $\mathbf{j}_s$, and for small $\mathbf{j}_s$ it equals $T\mathbf{j}_s$, in accordance with the well-known relation linking $\mathbf{q}$ and $\mathbf{j}_s$. In the nonequilibrium fluid, the entropy flux $\mathbf{j}_s$ (or heat flux $\mathbf{q}$) is coupled with the hydrodynamic velocity field as the term $(g\tilde{\rho}^{\,-1}\mathbf{j}_s\mathbf{j}_s)\cdot\mathbf{u}=g\tilde{s}(\mathbf{u}\cdot\mathbf{v}_s)$ in Eq. (75) indicates. For $g=0$, the momentum balance equation (70) simplifies to the case of that for the equilibrium perfect fluid, but the effect of heat flow still persists in the energy balance equation (75). Recovering Eulerian fluid theory requires not only taking $g=0$ in our theory, corresponding to an equilibrium fluid description, but also imposing the condition $\mathbf{j}_s=0$ in the equations of the entropy balance and the density of the entropy flux, Eqs. (43) and (72). However, this is also a natural physical requirement for equilibrium, since $\mathbf{j}_s$ is taken as an independent variable.

VIII. INVARIANT NONEQUILIBRIUM QUANTITIES AND THE SIGNIFICANCE OF THERMAL MOMENTUM

We verified that the stationary Lagrangian Λ, the components of energy-momentum tensor G^{jk}, and the corresponding balance laws remain the same when the heat flux $\mathbf{q}$ or the thermal momentum $\mathbf{i}_s$ are used instead of entropy flux $\mathbf{j}_s$ in the action functional (46) based on the kinetic potential (41). While this fact is not a surprise in view of invariance properties of any variational problem, its physical consequences cannot be underestimated, since it indicates how natural and "objective" are the nonequilibrium thermodynamic quantities appearing in Λ and G^{jk}. This objectivity may be contrasted with the arbitrariness of the "nonequilibrium temperatures and pressures" discussed in Sec. II, such as those given by Eqs. (30) and (31). These depend on the type of nonequilibrium variable ($\mathbf{q}$, $\mathbf{j}_s$, $\mathbf{i}_s$, $\mathbf{a}_s$, etc.), which is kept constant when differentiating the nonequilibrium energy $\tilde{e}$. Therefore, special attention should be given to the nonequilibrium quantities appearing in G^{jk}, Λ, and the balance laws. They pertain to the point A in Fig. 1, and are [with the correct lower sign as retained in Eqs. (67), (73), and (74)]

$$\tilde{P}(\tilde{\rho},\tilde{s},\mathbf{j}_s)=P_{(B)}(\tilde{\rho},\tilde{s})-\tfrac{1}{2}(\partial g/\partial\tilde{\rho})_s J_s^2=\hat{\Lambda} \;, \qquad (76)$$

$$\tilde{T}(\tilde{\rho},\tilde{s},\mathbf{j}_s)=T_{(B)}(\tilde{\rho},\tilde{s})-\tfrac{1}{2}\tilde{\rho}^{\,-2}(\partial g/\partial s)_\rho j_s^2 \;, \qquad (77)$$

$$\tilde{e}(\tilde{\rho},\tilde{s},\mathbf{j}_s)=e_{(B)}(\tilde{\rho},\tilde{s})+\tfrac{1}{2}(g\tilde{\rho}^{\,-1}j_s^2) \;. \qquad (78)$$

The last result recovers our starting point, Eqs. (3) and (24), for arbitrary $g(\rho,s)$. The interpretation of $\tilde{T}$, Eq. (77), as the nonequilibrium temperature of the system at state A follows immediately from the energy flux expression, Eq. (72). Since for the resting fluid ($\mathbf{u}=0$) the only contribution to the energy flux must be the heat flux, it is clear that the invariant expression $[T_B-\tfrac{1}{2}\tilde{\rho}^{\,-2}(\partial g/\partial s)j_s^2]\mathbf{j}_s$ in Eq. (75) must represent the heat flux density $\mathbf{q}$. The nonequilibrium temperature $\tilde{T}$, Eq. (77), is therefore the invariant coefficient linking the heat-flux density [$\Omega=\mathbf{q}$ at $\mathbf{u}=0$] with the entropy flux density $\mathbf{j}_s$, i.e., $\tilde{T}=\Omega_{\mathbf{u}=0}/\mathbf{j}_s$. This is identical with the dynamical definition of the temperature written symbolically in the term $T=e'/s'$ postulated sometimes with the requirement that it should coincide with the thermodynamic derivative $(\partial\tilde{e}/\partial\tilde{s})_v$. Since, however, the value of such a derivative depends on the nonequilibrium variable ($\mathbf{j}_s$, $\mathbf{i}_s$, etc.) used when differentiating $\tilde{e}$ with respect to $\tilde{s}$, the fundamental questions arise as to which nonequilibrium variable should be kept constant in the nonequilibrium energy (78) so that the partial derivative $\partial\tilde{e}/\partial\tilde{s}$ yields the temperature (77). It is easy to verify that $\mathbf{j}_s$ and $\mathbf{q}$ are not appropriate variables in this regard and the correct variable is the thermal momentum variable $\mathbf{i}_s$, Eq. (29b). Indeed, expressing the energy $\tilde{e}$ in terms of $\mathbf{i}_s$ yields

$$\tilde{e}(\tilde{\rho},\tilde{s},i_s)=e_{(B)}(\tilde{\rho},\tilde{s})+\mathbf{i}_s^2/2g \ , \tag{79}$$

and the partial derivative $(\partial\tilde{e}/\partial\tilde{s})_{\rho,i_s}$ is just Eq. (77). Furthermore, the differentiating of $\tilde{e}$ with respect to $-\rho^{-1}$ (or $-\tilde{V}$) yields the nonequilibrium pressure of the system at the point A, which coincides with the expression (76) and hence the stationary Lagrangian $\hat{\Lambda}$.

This coincidence is, of course, an attractive property of the variational approach in view of the invariance property of the Lagrangian Λ and the physical pressure with respect to transformation of both thermodynamic and space-time coordinates. In addition, with the expression (76) a subtle point can be resolved. In the kinetic theory, the nonequilibrium pressure is as a rule defined as one-third of the trace of the nonequilibrium pressure tensor[22]

$$\underline{P}=\int mCC\tilde{f}\,d\mathbf{c} \ , \tag{80}$$

which corresponds with the following expression in Eq. (70):

$$\begin{aligned}\underline{P}&=\underline{1}[P_{(\beta)}-\tfrac{1}{2}(\partial g/\partial\rho)j_s^2]+\tilde{\rho}g\tilde{s}^{\,2}\mathbf{v}_s\mathbf{v}_s\\ &=\underline{1}\tilde{P}+\rho'\mathbf{v}_s\mathbf{v}_s \ ,\end{aligned} \tag{81}$$

with $\rho'\equiv\tilde{\rho}g\tilde{s}^{\,2}$. Our pressure (76), or the stationary Lagrangian $\hat{\Lambda}$, is thus one-third of the trace of $\underline{P}$ minus $\frac{1}{3}\tilde{\rho}g\tilde{s}^{\,2}v_s^2$ (or minus $\frac{1}{3}\mathrm{Tr}(\rho'\mathbf{v}_s\mathbf{v}_s)$ rather than $\frac{1}{3}\mathrm{Tr}\underline{P}$ itself. This indicates that, in the local nonequilibrium case, the entropy flow stress $-\rho'\mathbf{v}_s\mathbf{v}_s$ should be deducted from the pressure tensor based on the disequilibrium definition. Indeed, it is the "ordered-flow"-type term rather than the chaos-related thermodynamic term. Its separation from the pressure tensor $\underline{P}$, Eq. (80), is just as natural as separating the hydrodynamic term $\rho\mathbf{u}\mathbf{u}$ in Eq. (70) or the mass diffusion terms $\rho_k\mathbf{v}_k\mathbf{v}_k$ ($\mathbf{v}_k$ is the diffusion velocity of the kth species) from the definition of $\underline{P}$, Eq. (80), in multicomponent systems; see, e.g., Truesdell[23] for a definition of the pressure P as $\frac{1}{3}\mathrm{Tr}(\underline{P}-\sum_k\rho_k\mathbf{v}_k\mathbf{v}_k)$ in this case. Our approach singles out the role of diffusional stresses in momentum equations and the corresponding "kinetic energy of diffusion" $\frac{1}{2}g\tilde{\rho}^{-2}j_s^2$ in energy equations associated with the flow of heat or entropy.

The virtue of recognizing the nonequilibrium variables ($\tilde{e}$, $\tilde{T}$, and $\tilde{P}$) pertaining to the actual physical state (point A, Fig. 1) lies in the fact that the balance equations expressed in terms of these variables are not only simplest but also take an objective form independent of the representation used. This occurs because the parameters of the arbitrary reference equilibrium states (B, C, or D; Fig. 1), which depend on the variables used in the thermodynamic description, do not appear in the objective balance laws. The representation-free form of the balance equations (70) and (75) is, respectively,

$$\partial\tilde{\rho}\mathbf{u}/\partial t+\nabla\cdot(\tilde{\rho}\mathbf{u}\mathbf{u}+\underline{1}\tilde{P}+\underline{\pi})-\tilde{\rho}\mathbf{F}=\mathbf{0} \ , \tag{82}$$

$$\partial\tilde{\rho}(\tilde{e}+u^2/2+\psi)/\partial t+\nabla\cdot[\tilde{\rho}\mathbf{u}(\tilde{h}+u^2/2+\psi)+\tilde{T}\mathbf{j}_s+\underline{\pi}\cdot\mathbf{u}] \\ -\tilde{\rho}(\partial\psi/\partial t)=0 \tag{83}$$

(all quantities pertain here to point A). Here $\underline{\pi}=g\rho^{-1}\mathbf{j}_s\mathbf{j}_s=\tilde{\rho}g\tilde{s}^{\,2}\mathbf{v}_s\mathbf{v}_s$ is the previously discussed entropy flow contribution to the pressure tensor $\underline{P}$ and $\underline{\pi}\cdot\mathbf{u}$ the corresponding power. Although this form of balance law resembles precisely that known from the description of fluids in local equilibrium, it should be remembered that the quantities $\tilde{e}$, $\tilde{P}$, and $\tilde{T}$ are flux dependent in our nonequilibrium case. The splitting of these quantities into the sum of the parameters of the reference equilibrium state (B, C, or D; Fig. 1) and nonequilibrium flux correction is always representation dependent—the price paid by one who wants to use the well-known equilibrium data in disequilibrium situations. Consequently, the basic equations of *nonequilibrium* fluids have forms dependent on the conventional thermodynamic variables used in the process description, and the nonequilibrium corrections appearing in one representation change or vanish in another representation. We omit here a detailed comparison of the balance laws in various representations (this problem is planned to be discussed elsewhere by the authors); see Sec. IX where some comparison is done for the particular case of the ideal gas.

More remarks should be devoted to the thermal momentum variable, i.e., why does it turn out to be so essential? The answer is, because the basic entities in the Hamilton's principle are matter and entropy and the natural variables of the energy are their momenta or, in the Lagrangian, the corresponding velocities. Since the nonequilibrium thermal energy (24) is well defined, we have to expect to find the corresponding momenta as every Lagrangian approach requires. Thus we have not only velocities or momenta related to macroscopic (hydrodynamic) motion (velocity $\mathbf{u}$), but also to the diffusion of entropy or heat with relative velocity $\mathbf{v}_s$. In the multicomponent case, one would have also diffusion velocities $\mathbf{v}_k$ for individual species and the "internal momenta of unit mass" $\mathbf{v}_k$. For our one-component fluid, the momenta pertaining to the unit mass or unit entropy are obtained by differentiating the unit mass Lagrangian $L/\tilde{\rho}$ or the unit entropy Lagrangian $L/\tilde{\rho}\tilde{s}$ with respect to appropriate velocity

$$\partial(L/\tilde{\rho})\partial\mathbf{u}=\partial L/\partial\mathbf{J} \ , \tag{84}$$

$$\partial(L/\tilde{\rho}_s)/\partial\mathbf{v}_s=\partial L/\partial\mathbf{j}_s=\mathbf{i}_s \ . \tag{85}$$

These definitions are general and pertain to arbitrary L, classical or relativistic. In the particular case of the Lagrangian (41),

$$\partial L/\partial\mathbf{J}=\mathbf{u} \ , \tag{86}$$

$$\partial L/\partial\mathbf{j}_s=\mathbf{i}_s=\tilde{\rho}^{-1}g\,\mathbf{j}_s \ . \tag{87}$$

The relative (non-absolute) nature of the velocity $\mathbf{v}_s$ is explained by viewing the heat as the transfer of energy or entropy in the *fluid frame*. Our earlier definition of $\mathbf{i}_s$ as the derivative $\partial\tilde{\rho}\tilde{e}/\partial\mathbf{j}_s$ (volumetric entropy flux adjoint) conformed to the general definition (85), but it was more specific; it was, in fact, restricted to Lagrangian quadratic in $\mathbf{v}_s$ (or $\mathbf{j}_s$) having a form unaffected by external vector fields (e.g., magnetic field). For so simple a Lagrangian L, which was our case with heat flow, $\mathbf{i}_s$ and $\mathbf{j}_s$ are proportional; this is why our heuristically stated transformation

(38) survived in the case of $\mathbf{j}_s$. In more general cases only $\mathbf{i}_s$ should appear in Eq. (38), which is the natural variable of the energy function. The use of $\mathbf{a}_s$, although also allowable in our case in the Legendre transformation, Eq. (38), is less appropriate than the use of $\mathbf{i}_s$ from the viewpoint of the Gibbs equation describing $\tilde{e}$ or $\widetilde{\rho e}$, since $\mathbf{a}_s$ does not generate the invariant pressures and temperatures, Eqs. (76) and (77), and $\mathbf{i}_s$ does. This proves that despite the simple relation $\mathbf{a}_s=\rho^{-1}\mathbf{i}_s$, Eq. (29), it is the thermal momentum variable $\mathbf{i}_s$ obeying the general definition (85) and not the entropy flux adjoint $\mathbf{a}_s$ based on the more special definition, Eqs. (13) or (29), which plays the fundamental role in the energy function Eq. (79) and corresponding Gibbs equation. This is what one would expect comparing the dimensions of $\mathbf{i}_s$, the momentum per unit entropy, and $\mathbf{a}_s$, the momentum per unit entropy multiplied by the volume of mass unit—a far less physically intuitive dimension. The thermal momentum $\mathbf{i}_s$ defined by Eq. (85) is, with accuracy to the arbitrary constant multiplier, the only variable, which by Legendre transformation from the given Lagrangian L, yields the correct energy formula and invariant nonequilibrium thermodynamic parameters, Eqs. (76) and (77), by differentiation of $\tilde{e}$ Eq. (79). It is easy to verify that for our Lagrangian, Eq. (41), since $\partial L/\partial\mathbf{J}=\mathbf{u}$, the Legendre transform yields

$$\begin{aligned}\widetilde{E}(\tilde{\rho},\tilde{s},\mathbf{u},\mathbf{i}_s)&=(\partial L/\partial\mathbf{J})\cdot\mathbf{J}+(\partial L/\partial\mathbf{j}_s)\cdot\mathbf{j}_s-L\\&=\tilde{\rho}e(\tilde{\rho},\tilde{s})+\tfrac{1}{2}\tilde{\rho}g^{-1}i_s^2+\tfrac{1}{2}\rho u^2+\rho\psi\ .\end{aligned}\tag{88}$$

This is the correct total energy (32) in terms of its natural[24] variables $(\tilde{\rho},\tilde{s},\mathbf{i}_s,\mathbf{u})$ containing the (volumetric) nonequilibrium internal energy $\widetilde{\rho e}$, (79). The inverse Legendre transformation applied to the function $\widetilde{E}(\tilde{\rho},\tilde{s},\mathbf{u},\mathbf{j}_s)$ allows one to recover the Lagrangian $L(\tilde{\rho},\tilde{s},\mathbf{u},\mathbf{j}_s)$, Eq. (41), from $\widetilde{E}$, Eq. (88). The Gibbs equations describing the specific and volumetric nonequilibrium internal energies $\tilde{e}$ or $\widetilde{\rho e}$, Eq. (79), are, respectively,

$$d\tilde{e}=\widetilde{T}d\tilde{s}-\widetilde{P}d\widetilde{V}+\tilde{\rho}^{-1}\mathbf{j}_s\cdot d\mathbf{i}_s\quad(\widetilde{P}=\widehat{\Lambda})\ ,\tag{89}$$

$$d(\widetilde{\rho e})=\widetilde{T}d\tilde{\rho}_s+\tilde{\mu}d\tilde{\rho}+\mathbf{j}_s\cdot d\mathbf{i}_s\ .\tag{90}$$

In this form, independent of the particular form of L, the above Gibbs equations are completely general and hold even for relativistic systems. Here $\tilde{\rho}_s=\widetilde{\rho s}$ and $\widetilde{T}$, $\widetilde{P}$, and $\tilde{\mu}$ are objective (invariant) nonequilibrium temperature, pressure, and chemical potential (at point A). Equations (76) and (77) describe $\widetilde{T}$ and $\widetilde{P}$ in terms of parameters $P_{(B)}$ and $T_{(B)}$ of the reference (isentropic and isochloric) state. The corresponding expression for $\tilde{\mu}$ is

$$\begin{aligned}\tilde{\mu}&=\tilde{e}+\widetilde{P}/\tilde{\rho}-\widetilde{T}\tilde{s}\\&=\mu_{(B)}(\tilde{\rho},\tilde{s})+\tfrac{1}{2}g\tilde{\rho}^{-2}\mathbf{j}_s^2[1-(\partial\ln g/\partial\ln\rho)_s\\&\qquad+(\partial\ln g/\partial\ln s)_\rho]\ .\end{aligned}\tag{91}$$

It is important to note that heat flux $\mathbf{q}$ can be found from our Gibbs equations (89) and (90) as

$$\mathbf{q}=\widetilde{T}\tilde{\rho}(\partial\tilde{e}/\partial\mathbf{i}_s)\ .\tag{92}$$

In a complementary paper we discuss the thermodynamic transformations related to the Gibbs equations (89) and (90) and the concept of nonequilibrium thermodynamic length.

IX. COMPATIBILITY WITH KINETIC THEORY

Let us return to the case of the ideal gas ($g=\text{const}$). The balance equations for the momentum and energy, Eqs. (70) and (75), respectively, differ in their form from those found in the kinetic theory.[6] Such differences are occasionally considered to be a proof of an inconsistency of extended thermodynamics or the restrictive nature of Hamilton's principle. It is believed by some that it holds only for equilibrium fluids.[2] Therefore, we are going to show that the compatibility with the balance equations of the kinetic theory is easily achieved if one takes into account the two different representations (energy and entropy) in which both descriptions are formulated. As Eq. (24) and Fig. 1 indicate, the equilibrium reference parameters of the two representations (points B and C) of the same nonequilibrium state A are connected by the following equations:

$$e_{(C)}=\tfrac{3}{2}kT_{(C)}/m=e_{(A)}=e_{(B)}(\tilde{\rho},\tilde{s})+\tfrac{1}{2}\rho^{-2}g\,\mathbf{j}_s^2\ ,\tag{93}$$

$$P_{(C)}=\rho kT_{(C)}/m=P_{(B)}(\tilde{\rho},\tilde{s})+\tfrac{1}{3}\tilde{\rho}^{-1}g\,\mathbf{j}_s^2\ ,\tag{94}$$

$$h_{(C)}=\tfrac{5}{2}kT_{(C)}/m=h_{(B)}(\tilde{\rho},\tilde{s})+\tfrac{5}{6}\tilde{\rho}^{-2}g\,\mathbf{j}_s^2\ ,\tag{95}$$

where $e_{(C)}$, $P_{(C)}$, and $h_{(C)}$ represent the energy, pressure, and enthalpies, respectively. Equation (76) indicates that in the ideal-gas case $\widetilde{P}=P_{(B)}$; hence from (94),

$$\widetilde{P}=P_{(C)}-\tfrac{1}{3}\tilde{\rho}^{-1}g\,\mathbf{j}_s^2=P_{(C)}-\tfrac{1}{3}\mathrm{Tr}\underline{\pi}\ .\tag{96}$$

Substituting this result into Eqs. (82) and (83) [equivalent to (70) and (75)], yields, since $\tilde{e}_{(A)}=e_{(C)}$,

$$\partial\tilde{\rho}\mathbf{u}/\partial t+\nabla\cdot(\tilde{\rho}\mathbf{u}\mathbf{u}+\underline{1}P_{(C)}+\underline{\Pi}\cdot\mathbf{u})-\tilde{\rho}\mathbf{F}=\mathbf{0}\ ,\tag{97}$$

$$\begin{aligned}&\partial\tilde{\rho}(e_{(C)}+u^2/2+\psi)/\partial t\\&\qquad+\nabla\cdot[\rho\mathbf{u}(h_{(C)}+u^2/2+\psi)+\mathbf{q}+\underline{\Pi}]-\tilde{\rho}\partial\psi/\partial t=0\ ,\end{aligned}\tag{98}$$

where

$$\underline{\Pi}=\underline{\pi}-\tfrac{1}{3}\underline{1}\,\mathrm{Tr}\underline{\pi}\tag{99}$$

is the symmetric *traceless* tensor describing shear stresses in the system. (Here they are caused only by the flow of heat; in the general case, macroscopic flow terms can contribute to $\underline{\Pi}$.) Nonequilibrium normal stresses associated with the definition of the nonequilibrium pressure used in the kinetic theory [$\tfrac{1}{3}\mathrm{Tr}\underline{P}$, where $\underline{P}$ is defined by Eq. (80)] do not appear in the case of the ideal gas. Equations (97) and (98) are the well-known balance laws obtained (in the entropy representation) in the kinetic theory.[6] The entropy representation form of Eqs. (97) and (98) of the ideal gas can be constructed with the energy representation form of Eqs. (70) and (75) taken for constant g. A natural extension of this work would be the inclusion of the momentum transport terms associated with the macroscopic motion (velocity field $\mathbf{u}$) and mass diffusion.

X. CONCLUSIONS

In classical fluid mechanics[25] the heat flux is as a rule only formally added to the energy flux of the perfect fluid in order to preserve an agreement of the theory with experiments and with kinetic theory.[6] Here we have shown that it can be derived as the expression $\tilde{T}\mathbf{j}_s$ if one allows the entropy flux to be associated with a degree of freedom independent of mass flow. In the traditional Eulerian fluid, the entropy can be transported only by the convection of the mass elements and the heat flux cannot appear. In other words, in the Eulerian fluid the entropy is "stuck" to the individual particles of the fluid, and the heat, interpreted as the effect of the entropy flow in the fluid frame, cannot exist. Making entropy flux an unconstrained variable allows entropy to flow freely, independently of mass, so that heat flow appears naturally. However, when the entropy flow becomes unconstrained, it becomes at the same time elevated to the rank of an additional independent flow variable. This is why the $\mathbf{j}_s$ variable and corresponding thermal momentum $\mathbf{i}_s$ are so significant in the Legendre transformation, Eq. (38), and in the extension of Hamilton's principle to nonequilibrium fluids. The compatibility of our results with the kinetic theory pertains to the Grad formalism rather than Chapman-Enskog formalism. This compatibility proves that the extension of Hamilton's principle to nonequilibrium fluids is possible, provided that a careful analysis of the nonequilibrium availability is made and the relation between the two representations of thermodynamics, the entropy and energy representations, is properly understood in the case of nonequilibrium. Furthermore, the invariance of the nonequilibrium thermodynamic quantities, Eqs. (76)–(78), revealed by the variational approach, makes it possible to prove the essential role of the thermal momentum $\mathbf{i}_s = \partial L / \partial \mathbf{j}_s$ as the natural nonequilibrium variable in the Gibbs equation describing fluid with heat and to solve simultaneously the problem of nonequilibrium temperatures and pressures.

ACKNOWLEDGMENTS

We acknowledge the support of the U.S. Department of Energy, under Contract No. DOE-FG02-86ER13488.

APPENDIX: IRREVERSIBLE HEAT CONDUCTION

In the case of irreversible processes, the conservation laws for mass, momentum, and energy constitute the constraints on the entropy balance equation (with a positive source σ).

$$\partial \tilde{\rho} \tilde{s} / \partial t + \nabla \cdot (\mathbf{J} s + \mathbf{j}_s) = \sigma \ . \tag{A1}$$

Starting with these conservation laws given as Eqs. (42), (70), and (75), an expression for the rate of entropy σ has been obtained in the form

$$\sigma = -T \mathbf{j}_s \cdot \left[\frac{\partial (g \tilde{s} \mathbf{v}_s)}{\partial t} + \nabla T + \nabla g \tilde{s} (\mathbf{u} \cdot \mathbf{v}_s) \right] . \tag{A2}$$

Note that the time derivative of $\mathbf{i}_s = g\tilde{s}\mathbf{v}_s$, rather than $\mathbf{q}$ or $\mathbf{j}_s$, appears in this equation. For local equilibrium one can put $g = 0$ in the above result and recover the classical expression for the entropy production. In order to interpret expression (A2) from the physical viewpoint, one can eliminate the Lagrangian multiplier from the reversible stationarity conditions, Eqs. (49) and (50), and obtain

$$(\partial/\partial t)(\partial L / \partial \mathbf{j}_s) - \nabla [\partial L / \tilde{\rho} \partial \tilde{s} + \mathbf{u} \cdot (\partial L / \partial \mathbf{j}_s)] = 0 \ . \tag{A3}$$

But this is precisely the expression in the large parentheses of Eq. (A2) for our L. Hence, for the irreversible process one may write

$$T\sigma = -\mathbf{j}_s \cdot (\partial/\partial t)(\partial L / \partial \mathbf{j}_s) - \nabla (\partial L / \tilde{\rho} \partial \tilde{s} + \mathbf{u} \cdot \partial L / \partial \mathbf{j}_s)] \ , \tag{A4}$$

or verbally, (dissipation function) = −(irreversible flux) × (reversible variational force). Thus we have obtained the generalized thermodynamic force as the reversible force derived from Hamilton's formalism. An analogous result occurs in lumped-parameter systems where the entropy source is the sum of the products of irreversible flows and the variational derivatives, i.e., the left-hand side of the Euler equations.[26] When the Lagrangian is independent of rates (or fluxes), the expressions mentioned above become usual gradients which correspond with the local equilibrium theory.

Whenever the effect of g, Eq. (25), can be neglected ($g = 0$), Eq. (A2) gives $\sigma = -\mathbf{j}_s \nabla \ln T$; hence one may postulate that $\mathbf{j}_s = -\tilde{\lambda} \nabla \ln T$, or after multiplying by T,

$$\mathbf{q} = -\tilde{\lambda} \nabla T \ , \tag{A5}$$

which is the Fourier law with the heat conductivity coefficient $\tilde{\lambda}$. However, for nonzero g, Eq. (A2) is a better approximation of the real situation. For the isobaric fluid at rest ($\mathbf{u} = 0$, $P = \text{const}$), Eq. (A2) implies

$$\mathbf{j}_s = -\tilde{\lambda} T^{-1} (\partial \mathbf{i}_s / \partial t + \nabla T) \ , \tag{A6}$$

exhibiting clearly the role of the thermal momentum in the extended phenomenological law. Substituting this result with $\mathbf{q} = T \mathbf{j}_s$ and using the ideal-gas equation in the expression $\mathbf{j}_s = g \rho^{-1} \mathbf{q} T^{-1}$, one obtains without any approximations the Cattaneo equation for an isobaric gas

$$\mathbf{q} = -\tilde{\lambda} (gk / mP)(\partial \mathbf{q} / \partial t) - \tilde{\lambda} \nabla T \ . \tag{A7}$$

The thermal relaxation time τ can be introduced, which, on the basis of Eqs. (A7) and (26), is

$$\tau = \tilde{\lambda} gk / mP = 2\tilde{\lambda} m / 5kP \ . \tag{A8}$$

This value of τ is in complete agreement with the kinetic theory.[1,6,7]

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