

## Canonical formalism, fundamental equation, and generalized thermomechanics for irreversible fluids with heat transfer

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(Received 3 June 1992)

A Lagrangian with dissipative (e.g., Onsager's) potentials is constructed for the field description of irreversible heat-conducting fluids, off local equilibrium. Extremum conditions of action yield Clebsch representations of temperature, chemical potential, velocities, and generalized momenta, including a thermal momentum introduced recently [R. L. Selinger and F. R. S. Whitham, *Proc. R. Soc. London, Ser. A* **302**, 1 (1968); S. Sieniutycz and R. S. Berry, *Phys. Rev. A* **40**, 348 (1989)]. The basic question asked is "To what extent may irreversibility, represented by a given form of the entropy source, influence the analytical form of the conservation laws for the energy and momentum?" Nöther's energy for a fluid with heat flow is obtained, which leads to a fundamental equation and extended Hamiltonian dynamics obeying the second law of thermodynamics. While in the case of the Onsager potentials this energy coincides numerically with the classical energy  $E$ , it contains an extra term (vanishing along the path) still contributing to an irreversible evolution. Components of the energy-momentum tensor preserve all terms regarded standardly as "irreversible" (heat, tangential stresses, etc.) generalized to the case when thermodynamics includes the state gradients and the so-called thermal phase, which we introduce here. This variable, the Lagrange multiplier of the entropy generation balance, is crucial for consistent treatment of irreversible processes via an action formalism. We conclude with the hypothesis that embedding the first and second laws in the context of the extremal behavior of action under irreversible conditions may imply accretion of an additional term to the classical energy.

PACS number(s): 47.27.Te, 05.70.Ln, 44.10.+i

### I. INTRODUCTION

In this work we are describing heat flow in single-component fluids as a distributed variational problem in Eulerian or field representation. In such representation a definite region in space time (control volume in time) is observed rather than the definite fluid elements ("fluid particles"). Fluids are studied here in the most general irreversible case in which the thermal conductivity  $\kappa$  has a finite value. Theories for fluids without heat ("perfect fluids") or nonconducting fluids are known [1]. Treatments of fluids with infinite conductivity have been put forward [2,3] but exact variational principles for fluids with finite thermal conductivity are still unknown. Such principles must incorporate the second law within the action formalism. As we show here, this is possible only when the standard set of the thermodynamic variables is extended by including an extra variable  $\eta$ , which we call the thermal phase. This variable is the Lagrangian multiplier of the entropy constraint and, at the same time, the thermodynamic conjugate of the entropy source in an extended Gibbs equation [4].

Hamilton's principle for physical fields is studied in this work. It involves certain field variables, designated in general formulas by  $\mathbf{q}=(q_1, q_2, \dots, q_l, \dots, q_s)$ . They describe the system state which should be determined as functions of time  $t$  and position  $\mathbf{x}=(x, y, z)$ , or the space-time vector  $(\mathbf{x}, t)$ . We designate also this space-time vector as

$$\bar{\mathbf{x}}=(\mathbf{x}, t), \quad \text{where } \mathbf{x}=(x, y, z), \quad x_4=t.$$

The set of functions  $\mathbf{q}(\mathbf{x}, t)$  which make the distributed action  $A$  stationary obeys the Euler-Lagrange equations:

$$\begin{aligned} \frac{\delta \Lambda}{\delta q^1} &= 0, \\ \frac{\partial \Lambda}{\partial \mathbf{q}} - \nabla \cdot \frac{\partial \Lambda}{\partial \nabla \mathbf{q}} - \frac{\partial}{\partial t} \frac{\partial \Lambda}{\partial (\partial \mathbf{q} / \partial t)} &= 0 \end{aligned} \quad (1)$$

for  $q=(q^1, q^2, \dots, q^k, \dots, q^s)$ , and  $\delta \Lambda / \delta q^1$  are variational derivatives. The variational derivative of  $\Lambda$  is equal to the well-known partial derivative only for  $\Lambda$  independent of rates or gradients (a singular problem). Physics requires  $\Lambda$  to be dependent on the derivatives of  $q$ , meaning dependence of action  $A$  on the path (surface, configuration) chosen.

Since the conservation laws for the energy and momentum can be studied only via Hamilton's variational principles we do not consider in this work many other possible variational or extremum formulations for macroscopic processes [5-11] and others. A critical assessment of most of them is given in Finlayson's book [12].

Using Hamilton's variational principles has several benefits.

(1) Physical insight into the behavior of complicated phenomena can be acquired more easily from the laws describing a single scalar quantity (action, entropy, etc.) than from those in the form of the complicated sets of many differential equations.

(2) All components of the energy-momentum tensor of a distributed (e.g., hydrodynamic) system can be computed. Hence, exact conservation laws or, in nonconservative cases, balance laws, can be found from an exact Lagrangian  $\Lambda$ . Examples are classical mechanics and hydromechanics of perfect fluids where  $\Lambda$  is known.

(3) Unification of processes of various sorts, e.g., mechanical, electrical, and even chemical, even many complex multifold processes of biology, can be achieved.

(4) Estimates can be made of approximate solutions of various problems via direct variational methods and trial functions.

The most formidable difficulty is that, in general, the Lagrangians are unknown. For a majority of complex processes, especially for irreversible processes with reversible dynamical terms, no systematic rules are known so far to obtain the Lagrangians. An action integral (a functional) and the complete set of constraints are required for any exact variational formulation.

Here we construct rather than assume a Lagrangian describing irreversible processes of heat transfer, such that the second law is obeyed. Our method follows an original ideal of Serrin [13], who suggested that use of the more complex form of the energy side condition in a Lagrangian rather than that expressing adiabaticity of the perfect fluid should, perhaps, be helpful to treat complex, irreversible processes in fluids. The global Lagrangian of the thermal field  $\Lambda$  is the sum of the kinetic potential  $L$  and the scalar product of the constraint expressions and their Lagrange multipliers.

Such an approach looks like the standard one in the theory of perfect fluids [1] but it is not. First, our kinetic potential  $L$  is embedded in an enlarged space containing not only densities of matter and entropy,  $\rho$  and  $\rho_s$ , and the fluid velocity  $\mathbf{u} = \mathbf{J}/\rho$  (the classical variables) but also the velocity of the entropy transfer,  $\mathbf{u}_s = \mathbf{J}_s/\rho_s$ , where  $\mathbf{J}_s$  is the density of the total entropy flux. Second,  $L$  contains the (negative) product of the entropy source  $\sigma_s$  and its thermodynamic conjugate, the "thermal phase variable"  $\eta$ . The distinction between  $\mathbf{u}$  and  $\mathbf{u}_s$  preserves heat effects [1] and the explicit thermal phase  $\eta$  preserves the nonvanishing positive entropy source [4]  $\sigma_s = \partial L / \partial \eta$ . This allows one to develop a self-consistent variational treatment of real fluids in which the energy properties and conservation laws are investigated in terms of an expression describing the entropy source  $\sigma_s$ . In particular, the Onsager representation of  $\sigma_s$  as the sum of the two dissipation functions  $\Phi$  and  $\Psi$  can be used. However, other forms of  $\sigma_s$  preserving its positivity can also be tested.

Hence the basic goal of this work follows: to work out a self-consistent approach to heat flow in irreversible fluids containing the first and second laws of thermodynamics in the context of the extremal behavior of an action functional. The functional must preserve both energy conservation and entropy generation as consequence of its extremum.

The properties of the energy and momentum and the conservation laws in fluids conducting heat with a finite rate will be an important objective of our study. They are consequences of the objectivity of the action  $A$ . If the ac-

tion functional  $A[\mathbf{q}(\mathbf{x}, t)]$  is physical, then as an objective quantity it must be invariant with respect to the transformations of state and independent variables

$$A[\mathbf{q}(\tilde{\mathbf{x}})] = A[\mathbf{q}^*(\tilde{\mathbf{x}}^*)] \tag{2}$$

First Nöther's theorem specifies the invariance conditions for the action  $A[\mathbf{q}(\mathbf{x}, t)]$  with respect to the parallel translations in time and space (homogeneity of time and space)

$$\begin{aligned} \tilde{\mathbf{x}}^{*k} &= \tilde{\mathbf{x}}^k + \epsilon^k, \quad k = 1, 2, 3, 4, \\ q_l^* &= q_l, \quad l = 1, 2, \dots, s \end{aligned} \tag{3}$$

The homogeneity of time requires invariance of  $A$  with respect to (the one-parameter group of) time translations

$$\begin{aligned} t^* &= t + \epsilon, \quad -\infty < \epsilon < \infty, \\ \mathbf{x}^* &= \mathbf{x}, \\ \eta^* &= \eta, \quad \rho_s^* = \rho_s \dots, \\ \phi^* &= \phi, \quad \rho^* = \rho \dots \end{aligned} \tag{3a}$$

where  $\eta, \rho$ , etc. are various field variables, components of  $q$ . Their complete set in our heat transfer case will be defined later. Equation (3a) says change of the initial time does not change the system behavior if external fields are absent so that the system is autonomous and isolated. This leads to the conservation of the energy.

The homogeneity of space requires the invariance of  $A$  with respect to (the three-parameter group of) space translations

$$\begin{aligned} t^* &= t, \\ \mathbf{x}^* &= \mathbf{x} + \epsilon, \quad -\infty < \epsilon^\alpha < \infty, \quad \alpha = 1, 2, 3, \\ \eta^* &= \eta, \quad \rho_s^* = \rho_s \dots, \\ \phi^* &= \phi, \quad \rho^* = \rho \dots \end{aligned} \tag{3b}$$

This leads to the conservation of the linear momentum.

The isotropy of space requires the invariance of  $A$  with respect to (the three-parameter group of) rotations  $\mathbf{x}^{str} = \mathbf{R}(\epsilon^1, \epsilon^2, \epsilon^3) \cdot \mathbf{x}$  where  $\mathbf{R}$  is a rotation matrix depending on the Eulerian angles. It leads here to the conservation of angular momentum since the micropolar effects are ignored. There are also internal symmetries (gauge groups) related with the impossibility of fixing a phase variable  $\phi$  by an experiment; these lead to the total mass conservation. They are important in the reacting multicomponent systems which are not considered here [14].

The invariance conditions of  $A$  are the conservation equations for the following energy-momentum tensor:

$$G^{ji} = \sum_l \frac{\partial q_l}{\partial \tilde{x}_j} \frac{\partial \Lambda}{\partial (\partial q_l / \partial \tilde{x}_k)} - \delta^{jk} \Lambda \tag{4}$$

( $\delta^{jk}$  is the Kronecker delta). They describe the vanishing four-divergences ( $\text{div}, \partial / \partial t$ ) of  $G^{jk}$  of the general structure

$$G = \begin{pmatrix} T & -\Gamma \\ Q & E \end{pmatrix}, \tag{5}$$

where  $T$  is the stress tensor,  $\Gamma$  is the momentum density,  $Q$  is the energy flux density, and  $E$  is the total energy density. The components of this tensor are well known for a fluid conducting heat ideally [2] and for the adiabatic fluid where heat is absent, the "perfect fluid" [15].

When external fields are present, only the balance equations result:

$$\sum_k \left( \frac{\partial G^{jk}}{\partial \bar{x}_k} \right) + \frac{\partial \Lambda}{\partial x_j} = 0 \quad (6)$$

for  $j, k = 1, 2, 3, 4$ . As shown here one can go to the tensor  $G$  and hence to conservation laws direction from the total energy density  $E$ , or by transforming this energy into the kinetic potential  $L$ . In principle any thermodynamic potential (TP) in its natural variables [16] can be used, although some are easier to use than others. This is represented by the scheme

$$\begin{pmatrix} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & E \end{pmatrix} \xrightarrow{\text{Legendre tr.}} \begin{pmatrix} T^{11} & T^{12} & T^{13} & -\Gamma^1 \\ T^{21} & T^{22} & T^{23} & -\Gamma^2 \\ T^{31} & T^{32} & T^{33} & -\Gamma^3 \\ Q^1 & Q^2 & Q^3 & E \end{pmatrix}, \quad (7)$$

$E \rightarrow \rightarrow \text{any TP} \rightarrow \rightarrow$

The plan of our analysis is as follows. The dissipative Lagrangian, constraints, and action  $A$  are introduced in Sec. II. Extremum conditions on  $A$  (Sec. III) show the importance of Clebsch variables (Lagrange multipliers of mass and entropy balances) for "gradient representations" of the temperature  $T$ , chemical potential  $\mu$ , and the generalized momenta  $\mathbf{p}$  and  $\mathbf{p}_s$  associated with the velocities  $\mathbf{u}$  and  $\mathbf{u}_s$ . These gradient representations emerge as natural consequences of the fact that the generalized momenta are the derivatives with respect to velocities of the kinetic potential  $L$ , and the nonequilibrium thermodynamic intensities ( $T, \mu$ ) are the negative derivatives of  $L$  with respect to the densities of the entropy and matter,  $\rho_s$  and  $\rho$ . The latter property is necessary for consistency with equilibrium theory. (Note that these definitions of  $T$  and  $\mu$  are automatically obeyed in the equilibrium case where  $L = -\rho e_{\text{eq}}$  and that in a general case, functional derivatives rather than partial derivatives are used.) Sections V and VI show that the preassigned dissipation (given  $\sigma_s$ ) may change energy and momenta. Although in the case of Onsager potentials numerical agreement with classical energy can be achieved, this energy is a nonclassical function of the generalized momenta, yielding irreversible equations of motion. The related entropy production is equal to the derivative  $\partial E / \partial \eta$ . The gradient representation of this energy is studied in Sec. VI where the components of the energy-momentum tensor are found. They contain terms usually regarded as "irreversible" (heat  $\mathbf{q}$ , stress  $\Pi$ , work  $\Pi \cdot \mathbf{u}$ , etc.). In Sec. VII the irreversibility of the heat transfer equations is shown. The effect of the thermal phase  $\eta$  on the conservation laws of the energy and momentum is discussed in Sec. VIII. Section IX treats the role of thermodynamic poten-

tials in various representations of the general Lagrangian  $\Lambda$ . We show that independent variations of both (extended) state variables and their thermodynamic conjugates are natural. Section X demonstrates the canonical structure of equations of motion in the Clebsch space of the densities and phases and the related benefits allowing transformations to various noncanonical variables ("physical variables") via the theory of Poisson brackets. Section XI calls for tests of various (non-Onsagerian) expressions for entropy sources, and Section XII summarizes our results. A relevant statement of the symmetry and conservation considerations for this work was made by Callen [16] in pp. 460–462 of his text.

## II. A LAGRANGIAN WITH DISSIPATIVE POTENTIALS AND CONSTRAINTS

We consider a single-component fluid of density  $\rho$ , specific entropy  $s$  (entropy density  $\rho_s$ ), and velocity  $\mathbf{u}$ . An essential difference in treating the fluids with heat and the perfect fluids (where the notion of heat is absent) is caused by the fact that, in the fluids with heat the entropy can flow even if the matter is at rest or the matter flow is constrained in an arbitrary way. Exploiting this notion, we showed [2] that for the treatment of heat problems it is enough to assume that the flow of the entropy is an independent variable in Hamilton's principle. This is a natural extension of the principle which suggests what to use in an action functional, the total entropy flux  $\mathbf{J}_s = \rho_s \mathbf{u} + \mathbf{j}_s$ , rather than its convective component  $\rho_s \mathbf{u}$  only. The convective component plays a role in the theory of the perfect fluid, causing the changes of the entropy (at a definite point of the physical space) due to flow of the fluid, even if the individual fluid particles do not exchange the heat. The heat exchange between the particles in real fluids is attributed to the  $\mathbf{j}_s$  part of the entropy flux, the conductive part. The specific internal energy  $e$  contains the contribution of  $\mathbf{j}_s$  known from the statistical mechanics [17–19]. It may be expressed as [2]

$$e(\rho, \rho_s, \mathbf{j}_s) = e^{\text{eq}}(\rho, \rho_s) + \frac{1}{2} \rho^{-2} g(\rho, \rho_s) \mathbf{j}_s^2, \quad (8)$$

where  $g(\rho, \rho_s)$  is an "inertial function" defined below. The related kinetic potential of the fluid conducting heat perfectly, which uses the Legendre transform of  $\rho e$ , is

$$L^0 = \frac{1}{2} \rho \mathbf{u}^2 + \frac{1}{2} \rho^{-1} g(\rho, \rho_s) \mathbf{j}_s^2 - \rho(e + \Psi), \quad (9)$$

where  $\Psi = \Psi(\mathbf{x}, t)$  is a scalar potential describing an external field. Under the relaxation time approximation of the Boltzmann equation, the inertial function of the ideal gas can be found from the formula

$$g(\rho, \rho_s)^{\text{id gas}} = \frac{2m^2}{5k_B^2}, \quad (10)$$

where  $m$  is the mass of the hard-sphere particle and  $k_B$  is the Boltzmann constant. Hence the "inertial function"  $g$  of the ideal gas is constant. For real gases and fluids a generalization of the above expression is [2,20]

$$g(\rho, \rho_s) = T\rho / (c_p G), \quad (11)$$

where  $c_p$  is the specific heat capacity and  $G$  is the shear

modulus, equal to the pressure  $P$  in the case of the ideal gas. All the quantities must be expressed as functions of the densities of matter and entropy,  $\rho$  and  $\rho_s$ . Taking in Eq. (11)  $c_p = 5R/(2M) = 5k_B/(2m)$  and  $G = P = \rho k_B T/m$ , the ideal gas result, Eq. (10), is recovered. An alternative form of Eq. (11) also can be used [20],

$$g(\rho, \rho_s) = \tau T \rho / \kappa, \quad (12)$$

where  $\tau$  is the relaxation time and  $\kappa$  is the thermal conductivity. For the ideal gas  $\tau$  equals  $2\kappa m/(5k_B P)$  or  $2\kappa m^2/(5k_B^2 \rho T)$ , on the basis of the Clapeyron equation of state, and Eq. (12) yields Eq. (10). Equation (12) is less suitable than Eq. (11) since the relaxation time  $\tau$  is not readily available for real gases and fluids. Equations (12) and (11) yield the well-known formula for the thermal relaxation time,  $\tau = D_s \rho / G = D_s / c_0^2$ , where  $c_0 = (G/\rho)^{1/2}$  is the so-called thermal propagation speed and  $D_s = \kappa/(\rho c_p)$  is the heat diffusivity.

It should be remembered that we pursue a macroscopic theory which presumably has a microscopic underlying basis. In fact, the origin of the kinetic potential, Eq. (9), is in kinetic theory, where, as already said, Grad's (1958) moment solution [17] of the Boltzmann equation is essential. Once  $L^0$  is formulated, however, it is a very suitable starting point for describing heat transfer away from local equilibrium, even for dense gases and polyatomic fluids. Thus Eq. (9) summarizes some important microscopic results in the manner suitable for the development of the macroscopic theory of continua with the heat transfer.

A canonical representation of the kinetic potential  $L$  and its constraints is used where the variables of the Lagrangian are the absolute velocities and densities. The constraint set will be taken in the standardized form involving the four-divergences (with  $\rho_s = \rho_s$ )

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (13)$$

$$\frac{\partial (\rho_s)}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s) = \sigma_s(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \mathbf{u}, \mathbf{u}_s), \quad (14)$$

where  $\mathbf{u} = \mathbf{J}/\rho$  and  $\mathbf{u}_s = \mathbf{J}_s/\rho_s$  are the absolute velocities of the transferred matter and entropy, respectively. In the framework of the Onsager theory the entropy source can depend on gradients of all the state variables; however, the gradients of the velocities are here ignored. We are interested mainly in heat transfer effects. Nevertheless some viscosity effects related to heat flow will still survive [2] (Sec. VIII).

The standardized constraints preserving the identity of the fluid and thermal elements are taken into consideration. In the sourceless case ( $\sigma_s = 0$ ) they are known from the theory of the perfect fluid [1], where  $\mathbf{u} = \mathbf{u}_s$ ,

$$\frac{\partial (\rho \alpha)}{\partial t} + \nabla \cdot (\rho \alpha \mathbf{u}) = 0, \quad (15)$$

$$\frac{\partial (\rho_s \alpha_s)}{\partial t} + \nabla \cdot (\rho_s \alpha_s \mathbf{u}_s) = 0. \quad (16)$$

From the viewpoint of that theory, these constraints are interpreted as the result of combining the constant initial

coordinate conditions  $d\alpha/dt = 0$  and  $d\alpha_s/dt = 0$  of the material and thermal elements with the (sourceless) continuity equations for the matter and entropy. It follows that generalization of these constraints to irreversible fluids is to some extent arbitrary. In Sec. III we show that this form of constraints can also be used for irreversible fluids (with sources), corresponding with  $\beta = 1$  in Eq. (20), and fading memory of the thermal Lagrangian coordinate  $\alpha_s$ .

To preserve a canonical formulation, *all* extensive variables in  $L$  should be used as densities rather than as specific quantities. The densities are  $\rho$ ,  $\rho_s = \rho s$ ,  $\gamma = \rho \alpha$ ,  $\gamma_s = \rho_s \alpha_s$ . Hence the constraint set in canonical form is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (13)$$

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s) = \sigma_s, \quad (14')$$

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot (\gamma \mathbf{u}) = 0, \quad (15')$$

$$\frac{\partial \gamma_s}{\partial t} + \nabla \cdot (\gamma_s \mathbf{u}_s) = 0. \quad (16')$$

In the case of multicomponent reacting fluids (not considered here) extra sources can appear in the mass continuity equations. However, regardless of any sources in Eqs. (13)–(16), their left-hand sides always preserve the same form of four-divergences. When these constraints are embedded into the Lagrangian  $\Lambda$ , the source terms are absorbed by the original (sourceless) kinetic potential  $L^0$ , Eq. (9), so that the resulting form of the kinetic potential  $L$  already has these sources incorporated. The case with sources therefore differs from the sourceless case by the presence in  $L$  of the Lagrange multiplier-type variables  $\phi$ ,  $\eta$ ,  $\lambda$ , and  $\lambda_s$ , associated with the constraints (13)–(16). In this case, these variables become elevated to the rank of the state variables.

The standardized Lagrangian  $\Lambda$  has the Stephens structure [15]

$$\Lambda_{\text{global}} = L + \mathcal{L} \cdot \mathbf{c} - \mathfrak{D} - \mathfrak{D}_s, \quad (17)$$

where  $\mathcal{L}$  represents Lagrange multipliers and  $\mathbf{c}$  represents constraints, and where  $\mathfrak{D}$  and  $\mathfrak{D}_s$  are the following four-divergence terms:

$$\mathfrak{D} = \frac{\partial (\rho \phi)}{\partial t} + \nabla \cdot (\rho \mathbf{u} \phi) \quad (18a)$$

and

$$\mathfrak{D}_s = \frac{\partial (\rho_s \eta)}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s \eta) \quad (18b)$$

containing the multipliers  $\phi$  and  $\eta$  of the mass and entropy balances. The subtracting of the four-divergences (18) means gauging of the Lagrangian. It does not change the equations of motion as Euler's equations of the variational problem. At the same time it provides direct elimina-

tion of the Lagrangian multipliers from the energy-momentum tensor of the limiting perfect fluid [15], and establishes the correspondence of this tensor to that developed for real fluids. We will call the action based on

$$\begin{aligned}
 A &= \int_{t_1}^{t_2} \Lambda dV dt \\
 &= \int_{t_1}^{t_2} \left[ L(\rho_i, \rho_s, \nabla \rho_i, \nabla \rho_s, \mathbf{u}_i, \mathbf{u}_s, \nabla \mathbf{u}_i, \nabla \mathbf{u}_s, \phi_i, \eta, \gamma_i, \gamma_s, \lambda_i, \lambda_s, \mathbf{x}, t) - \sum_i \rho_i \left[ \frac{\partial \phi_i}{\partial t} + \mathbf{u}_i \cdot \nabla \phi_i \right] \right. \\
 &\quad \left. - \rho_s \left[ \frac{\partial \eta}{\partial t} + \mathbf{u}_s \cdot \nabla \eta \right] - \sum_a \gamma_a \left[ \frac{\partial \lambda_a}{\partial t} + \mathbf{u}_i \cdot \nabla \lambda_a \right] - \gamma_s \left[ \frac{\partial \lambda_s}{\partial t} + \mathbf{u}_s \cdot \nabla \lambda_s \right] \right] dV dt
 \end{aligned} \tag{19}$$

(in relativistic descriptions and extended thermodynamic theories partial time derivatives may also appear in  $L$ ). The generalized kinetic potential  $L$  of this equation, with the source terms absorbed, has the structure

$$\begin{aligned}
 L &= L^0(\rho_i, \rho_s, \mathbf{u}_i, \mathbf{u}_s) \\
 &\quad - \sum_{i=1}^n \left[ \phi_i + \beta \frac{\lambda_i \gamma_i}{\rho_i} \right] \sigma_i(\rho_i, \rho_s, \mathbf{u}_i, \mathbf{u}_s) \\
 &\quad - \left[ \eta + \beta \frac{\lambda_s \gamma_s}{\rho_s} \right] \sigma_s(\rho_i, \rho_s, \mathbf{u}_i, \mathbf{u}_s),
 \end{aligned} \tag{20}$$

where  $L^0$  is the kinetic potential of the sourceless fluid and  $\sigma$  ( $\sigma_i, \sigma_s$ ) are the respective sources of the species and the entropy.

The coefficient  $\beta$  plays a formal role; it depends on the form of the identity constraints used in the action  $A$ . The constraints (15) and (16) or (15') and (16') correspond to  $\beta=0$  and a decay of the identity of the thermal paths. Another approach, assuming  $d\alpha/dt=0$  and  $d\lambda_s/dt=0$ , which follows that of the perfect fluid, corresponds to  $\beta=1$ . But then the generalized temperature and chemical potential of the theory depend on  $\lambda_i, \lambda_s, \gamma_i$ , and  $\gamma_s$ . This seems to be an unphysical property so the value  $\beta=0$  is assumed here, which leads to thermodynamic intensities independent of these quantities (see examples in Sec. III). It may be shown that taking  $\beta=0$  instead of  $\beta=1$  interchanges the properties of  $\gamma$  and  $\lambda$ . These quantities, in a sense, replace each other, preserving the same properties of the identity balances for the material and thermal elements of the fluid.

In our example we ignore a possible dependence of  $L$  on the velocity gradients and the related viscosity effects. (The functional rather than partial derivatives of the velocity  $\mathbf{u}$  would appear if these effects were important.) For the physical system considered here, a single-component fluid conducting the heat with a finite conductivity  $\kappa$ , the simplest action involves the simplified form of the general Lagrangian (20) taken for  $\beta=0$ ,

$$L = L^0 - \eta \sigma_s, \tag{21}$$

where  $L^0$  is the kinetic potential of the perfectly conducting fluid, Eq. (9), corresponding to the vanishing entropy source.

the Lagrangian (17) the standard action.

While multicomponent fluids are not considered here it is instructive to begin with a general standard action of a multicomponent fluid [14],

From Eqs. (9) and (21) the kinetic potential of a dissipative fluid with heat is

$$\begin{aligned}
 L &= \frac{1}{2} \rho \mathbf{u}^2 + \frac{1}{2} \rho_s^2 \rho^{-1} g(\rho, \rho_s)(\mathbf{u}_s - \mathbf{u})^2 \\
 &\quad - \rho [e(\rho, \rho_s) + \Psi(\mathbf{x}, t)] - \eta \sigma_s.
 \end{aligned} \tag{22}$$

The kinetic potential  $L^0$  of a fluid conducting heat ideally, Eq. (9), has been expressed in terms of the velocities and densities, the canonical variables of the Lagrangian. The same should be done for the entropy source  $\sigma_s$ .

The Onsager-Joule expression of the entropy source  $\sigma_s$  proportional to the  $\mathbf{j}_s^2$ ,

$$\begin{aligned}
 \sigma_s &= \mathbf{j}_s^2 / \kappa = \kappa^{-1} \rho_s^2 (\mathbf{u}_s - \mathbf{u})^2 \\
 &= (T\tau)^{-1} \rho_s^2 \rho^{-1} g(\rho, \rho_s)(\mathbf{u}_s - \mathbf{u})^2
 \end{aligned} \tag{23}$$

could be incorporated in  $L$  and hence in  $A$ , to be tested as an example. However, the use of the formula (23) in its original form is not obvious. It was already recognized by Onsager [5] in 1931 (although in the context of an entirely different variational approach which avoids the conservation laws) that, in order to preserve a physical kinetics, the entropy source has to be given in a specific way, expressing its functional representation. The two dissipation functions contributing to  $\sigma_s$  have to be used, so that  $\sigma_s = \Phi + \Psi$ . This occurs because it is the form of the source expression that is essential in variational calculus. The first dissipation function is velocity dependent. Its original representation in terms of the heat flux  $\mathbf{j}_q$  is transformed below into the Lagrangian representation variables used here:

$$\begin{aligned}
 \Phi(\rho, \rho_s, \mathbf{j}_s) &= \frac{1}{2} L^{-1}(\rho, \rho_s) \mathbf{j}_q^2 \\
 &= \frac{1}{2} (\kappa T^2)^{-1} \mathbf{j}_q^2 \\
 &= \frac{1}{2} \kappa^{-1} (\rho, \rho_s) \mathbf{j}_s^2 \\
 &= \frac{1}{2} \kappa^{-1} (\rho, \rho_s) \rho_s^2 (\mathbf{u}_s - \mathbf{u})^2.
 \end{aligned} \tag{24}$$

The second dissipation function is force dependent. Through the thermodynamic force  $\mathbf{X}$  (gradient of  $T^{-1}$  or its generalization) the function  $\Psi$  involves the derivatives of the extended state  $(\rho, \rho_s, \mathbf{u}, \mathbf{u}_s)$  with respect to the space-time variables  $(\mathbf{x}, t)$

$$\begin{aligned}
\Psi(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \partial \mathbf{j}_s / \partial t, \nabla \mathbf{j}_s) &= \frac{1}{2} L \mathbf{X}^2 = \kappa T^2 \left[ \nabla T^{-1} - \mathfrak{G}_q \cdot \frac{d \mathbf{j}_q}{dt} \right]^2 \\
&= \frac{1}{2} \kappa(\rho, \rho_s) \left[ -\nabla \ln T - \mathfrak{G}_s \cdot \frac{d \mathbf{j}_s}{dt} \right]^2 \\
&= \frac{1}{2} \kappa(\rho, \rho_s) \left[ c_v^{-1} \nabla \rho_s - \beta c_v^{-1} \nabla \rho + g_s \frac{d(\mathbf{u}_s - \mathbf{u})}{dt} \right]^2.
\end{aligned} \tag{25}$$

It is easy to see that the numerical values of these two dissipation functions are equal, i.e.,  $\Phi = \Psi$ , when the phenomenological equation for heat transfer holds (Onsagerian property). In Eq. (25)  $\mathfrak{G}_q$  is the positive inertial coefficient equal to the negative second derivative of the entropy with respect to the heat flux,  $-\partial^2 s / \partial \mathbf{j}_q^2$ ,  $\mathfrak{G}_s = T^2 \mathfrak{G}_q$ , and  $g_s = \mathfrak{G}_s \rho_s^{-1}$ . The expansion of  $\text{grad}(\ln T)$  in terms of the gradients of the entropy and matter results from the differential thermostatic formula (with accuracy to the level of the flux terms)

$$d\rho_s = c_v \frac{dT}{T} + \left[ \frac{\partial \rho_s}{\partial \rho} \right]_{T, V} d\rho \equiv c_v \frac{dT}{T} + \beta d\rho, \tag{26}$$

where  $\beta = \partial(\rho_s / \partial \rho)_{T, V}$  which equals  $s - k_B / m$  for the ideal gas. Hence the perfect differential of  $\ln T$

$$d \ln T = c_v^{-1} d\rho_s - \beta c_v^{-1} d\rho, \tag{27}$$

which has been used in Eq. (25). The heat capacity per unit volume  $c_v$  appears as  $\partial(\ln T / \partial \rho_s)^{-1}$  at constant  $\rho$ . The product of  $\kappa$  and  $c_v^{-1}$  is the well-known heat diffusivity  $D_s$ . This is a quasilinear description where all coefficients can be treated as functions of densities only, and these change on the time scale much slower than the velocities  $\mathbf{u}_s - \mathbf{u}$ .

In order not to expand formulas, in our examples we

assume that the coefficient  $g_s$  is small so that the acceleration term can be ignored, unless the thermal inertia have to be treated. In this case

$$\Psi(\rho, \rho_s, \nabla \rho, \nabla \rho_s) = -\frac{1}{2} \mathbf{j}_s \cdot \nabla \ln T = \frac{1}{2} c_v^{-1} D_s (\nabla \rho_s - \beta \nabla \rho)^2. \tag{28}$$

However, when thermal inertia are essential the substantive derivatives in Eq. (25) cannot be ignored. They have to be expressed in terms of partial time derivatives and the generalized momenta should be introduced as the functional rather than partial derivatives of  $L$  with respect to the velocities.

Another type of dissipation function is

$$\begin{aligned}
\Psi(\rho, \rho_s, \nabla \rho, \nabla \rho_s) &= -\frac{1}{2T} (\mathbf{j}_s \cdot \nabla T + \mathbf{j}_m \cdot \nabla \mu) \\
&= \frac{1}{2} c_v^{-1} \cdot \mathbf{D}_s : \nabla \rho \nabla \rho,
\end{aligned} \tag{29}$$

where  $\rho = (\rho, \rho_s)^T$  could be considered with  $\mathbf{j}_s$  and  $\mathbf{j}_m$  such that the sum of the corresponding diffusional momenta vanish. However, this form is ignored here; the most important conclusion results from Eq. (28). It is assumed that the multipliers  $\gamma$ ,  $\gamma_s$ ,  $\lambda$ , and  $\lambda_s$ , are not explicitly present in  $L$ . The standard action for a one-component fluid with heat is then

$$\begin{aligned}
A = \int & \left[ \frac{1}{2} \rho \mathbf{u}^2 + \frac{1}{2} \rho_s^2 \rho^{-1} g(\rho, \rho_s) (\mathbf{u}_s - \mathbf{u})^2 - \rho e(\rho, \rho_s) - \rho \Psi(x, t) - \eta \frac{1}{2} \kappa^{-1} \rho_s^2 (\mathbf{u}_s - \mathbf{u})^2 \right. \\
& - \eta \frac{1}{2} D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)^2 - \rho \left[ \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi \right] - \rho_s \left[ \frac{\partial \eta}{\partial t} + \mathbf{u}_s \cdot \nabla \eta \right] - \gamma \left[ \frac{\partial \lambda}{\partial t} + \mathbf{u} \cdot \nabla \lambda \right] \\
& \left. - \gamma_s \left[ \frac{\partial \lambda_s}{\partial t} + \mathbf{u}_s \cdot \nabla \lambda_s \right] \right] dV dt.
\end{aligned} \tag{30}$$

We remind the reader of the meaning of the Lagrangian multipliers or Clebsch variables [1,2]. The thermal phase  $\eta$  is the velocity potential of the entropy flow when this flow is irrotational. At the same time it is the Lagrangian action of the entropy element that has the initial velocity  $\lambda_s$ . The negative total time derivative of  $\eta$  is the non-equilibrium temperature. The matter phase  $\phi$  is the velocity potential when the fluid flow is irrotational and is at the same time the Lagrangian action of the fluid element that has the initial velocity  $\lambda$ . The negative total

time derivative of  $\phi$  is the nonequilibrium chemical potential.

### III. EXTREMUM CONDITIONS OF ACTION AND GRADIENT REPRESENTATIONS

The stationarity conditions of the functional (30) with respect to the multipliers  $\lambda$  and  $\lambda_s$  are Eqs. (15') and (16'):

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot (\gamma \mathbf{u}) = 0, \tag{15'}$$

$$\frac{\partial \gamma_s}{\partial t} + \nabla \cdot (\gamma_s \mathbf{u}_s) = 0. \quad (16')$$

They describe, for  $\gamma = \rho\alpha$  and  $\gamma_s = \rho_s \alpha_s$ , the identity behavior. For material trajectories,  $d\alpha/dt = 0$ , or

$$\frac{\partial \alpha}{\partial t} + \mathbf{u} \cdot \nabla \alpha = 0. \quad (31)$$

The identity of the thermal trajectories is decaying in this model ( $\beta = 0$ ). Indeed it results from Eqs. (14) and (16') that  $d \ln \alpha_s / dt = -\sigma_s / \rho_s$ , or

$$\frac{\partial \alpha_s}{\partial t} + \mathbf{u}_s \cdot \nabla \alpha_s = -\frac{\sigma_s \alpha_s}{\rho_s} \leq 0. \quad (32)$$

This means an exponential decay of  $\alpha_s$  for the constant entropy source per unit entropy, a sort of the relation describing the fading memory due to the thermal irreversibility.

The stationarity conditions of  $A$  with respect to the labels  $\gamma$  and  $\gamma_s$  describe the constancy of the multipliers  $\lambda$  and  $\lambda_s$  along the material and thermal paths

$$\frac{\partial \lambda}{\partial t} + \mathbf{u} \cdot \nabla \lambda = 0, \quad (33)$$

$$\frac{\partial \lambda_s}{\partial t} + \mathbf{u}_s \cdot \nabla \lambda_s = 0. \quad (34)$$

Modifying the entropy source term in  $L$ , Eq. (22), by the coefficient  $-(\eta + \lambda_s \gamma_s / \rho_s)$  replacing  $-\eta$ , a more traditional description would be obtained with  $\alpha_s$  constant but  $\lambda_s$  decaying. Perhaps an experiment comparing the difference in the nonequilibrium temperatures—the negative derivatives of  $L$  with respect to  $\rho_s$ —would reveal which model is better. We rely here on the functional (30) with the term  $-\eta \sigma_s$  only since it leads to a more reasonable nonequilibrium temperature, as the quantity independent of  $\lambda_s$  and  $\gamma_s$ .

The stationarity conditions of  $A$  with respect to phases  $\phi$  and  $\eta$  are the balance laws for mass and entropy

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = -\frac{\partial L}{\partial \phi} = 0, \quad (13)$$

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s) = -\frac{\partial L}{\partial \eta} = \Phi + \Psi. \quad (14'')$$

These describe, respectively, the conservation of mass and the entropy production or the sum of the two dissipation functions  $\Phi$  and  $\Psi$ .

The stationarity conditions of  $A$  with respect to the densities of the entropy and matter express the nonequilibrium thermodynamic intensities—the negative functional derivatives of  $L$  with respect to the corresponding densities—in terms of the gradients and time derivatives of corresponding phases  $\eta$  and  $\phi$ ,

$$T \equiv -\frac{\delta L}{\delta \rho_s} = -\left[ \frac{\partial \eta}{\partial t} + \mathbf{u}_s \cdot \nabla \eta \right], \quad (35)$$

$$\mu \equiv -\frac{\delta L}{\delta \rho} = -\left[ \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi \right]. \quad (36)$$

These are Clebsch representations of the thermodynamic intensities. For the dissipation model based on the Onsager potentials these intensities are

$$\begin{aligned} T(\rho_s, \rho, \eta) &= T^{\text{eq}}(\rho_s, \rho) - \frac{1}{2} \frac{\partial a}{\partial \rho_s} (\mathbf{u}_s - \mathbf{u})^2 \\ &+ \frac{1}{2} \frac{\partial b}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho)^2 \\ &- b \frac{\partial \beta}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho \\ &- \nabla \cdot [\eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)] \end{aligned} \quad (37)$$

and

$$\begin{aligned} \mu(\rho_s, \rho, \eta) &= \mu^{\text{eq}}(\rho_s, \rho) - \frac{1}{2} \rho \mathbf{u}^2 - \frac{1}{2} \frac{\partial a}{\partial \rho} (\mathbf{u}_s - \mathbf{u})^2 \\ &+ \frac{1}{2} \frac{\partial b}{\partial \rho} (\nabla \rho_s - \beta \nabla \rho)^2 + \Psi(x, t) \\ &- b \frac{\partial \beta}{\partial \rho} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho \\ &+ \nabla \cdot [\eta D_s c_v^{-1} \beta (\nabla \rho_s - \beta \nabla \rho)]. \end{aligned} \quad (38)$$

Here

$$a(\rho_s, \rho, \eta) \equiv \rho_s^2 [\rho^{-1} g(\rho, \rho_s) - \eta \kappa(\rho, \rho_s)^{-1}], \quad (39)$$

$$b(\rho_s, \rho, \eta) \equiv \eta D_s c_v^{-1} \quad (40)$$

are the resulting coefficients at the half squares of  $\mathbf{u}_s - \mathbf{u}$  and  $(\text{grad} \rho)^2$  in  $L$ . The thermodynamic intensities are always equal to the negative total time derivatives of the phases, the property which holds in this formalism for both equilibrium and nonequilibrium situations. The nonequilibrium temperatures and chemical potentials defined above in terms of  $L$  are the phase-dependent quantities having a nonlocal nature. From the properties of the canonical formalism for reversible processes (i.e., when the contribution of gradients of  $\rho_s$  and  $\rho$  is inessential)

$$T \equiv -\left[ \frac{\partial L}{\partial \rho_s} \right]_{\mathbf{u}} = \left[ \frac{\partial E}{\partial \rho_s} \right]_{\mathbf{p}}, \quad (41)$$

$$\mu \equiv -\left[ \frac{\partial L}{\partial \rho} \right]_{\mathbf{u}} = \left[ \frac{\partial E}{\partial \rho} \right]_{\mathbf{p}}. \quad (42)$$

It is easy to verify that these equations hold, in particular, for the case of the perfect fluid. They hold also for reversible nonequilibrium fluids conducting heat ideally [2,3]. Here they hold for the functional rather than usual partial derivatives, the consequence of the complex situation where the characteristic functions ( $L$ ,  $E$ , etc.) depend on the state gradients and the thermal phase  $\eta$ . The correspondence with the classical definitions of  $T$  and  $\mu$  is preserved provided that the total energy density  $E$  is expressed in terms of the generalized momenta rather than velocities.

The above definitions include the external potential; hence the explicit appearance of  $\Psi(\mathbf{x}, t)$  in the equation for  $\mu$ , identical to the way it appears in the definition of the electrochemical potential. However, external field

can be excluded from  $\mu$  if one wants to match requirements of the gauge invariance of the resulting energy-momentum tensor, forcing one to work with the kinetic potential  $L$  without this field. The external potential will then appear separately in the so-called interaction Lagrangian. The inclusion of external fields into definition of  $\mu$  causes the explicit dependence of the generalized thermodynamic potentials (Sec. IX) on space and time coordinates, representing the role of these fields. Such formalism is convenient when the external forces  $\mathbf{F}$  are needed; they can be obtained as the partial derivatives of the potentials with respect to  $\mathbf{x}$ , and their action can be taken into account in the single formalism.

The stationarity conditions of  $A$  with respect to the absolute velocities define the generalized (phase-dependent) momentum densities—the derivatives of  $L$  with respect to the transfer velocities—in terms of the gradients of the phases and labels. The thermal momentum density is

$$\begin{aligned} \mathbf{p}_s &\equiv \frac{\partial L}{\partial \mathbf{u}_s} \equiv a(\rho_s, \rho, \eta)(\mathbf{u}_s - \mathbf{u}) \\ &= \rho_s \nabla \eta + \gamma_s \nabla \lambda_s \end{aligned} \quad (43)$$

and the momentum density of matter

$$\begin{aligned} \mathbf{p} &\equiv \frac{\partial L}{\partial \mathbf{u}} \equiv \rho \mathbf{u} - a(\rho_s, \rho, \eta)(\mathbf{u}_s - \mathbf{u}) \\ &= \rho \nabla \phi + \gamma \nabla \lambda. \end{aligned} \quad (44)$$

This is the gradient representation of the momenta. We will show soon that, from Nöther's theorem, the total momentum density of the fluid  $\Gamma$  is the sum of  $\mathbf{p}$  and  $\mathbf{p}_s$  which yields  $\Gamma = \rho \mathbf{u}$ , the well-known result. Since the thermal momentum is finite, both the entropy flow and the flow of matter contribute to  $\rho \mathbf{u}$ . Therefore  $\mathbf{p} = \rho \mathbf{u} - \mathbf{p}_s$  is smaller than  $\rho \mathbf{u}$ , and the momentum  $\mathbf{p}$  may be called the bare momentum of the matter. The momen-

tum densities are no longer so simply related to the velocities as in the case of reversible processes.

Solving the above equations in terms of  $\mathbf{u}$  and  $\mathbf{u}_s$  yields the Clebsch (gradient) representations of the velocities

$$\begin{aligned} \mathbf{u} &= \frac{\mathbf{p} + \mathbf{p}_s}{\rho} \\ &= \frac{\rho \nabla \phi + \gamma \nabla \lambda + \rho_s \nabla \eta + \gamma_s \nabla \lambda_s}{\rho} \end{aligned} \quad (45)$$

and

$$\begin{aligned} \mathbf{u}_s &= \frac{\mathbf{p} + \mathbf{p}_s}{\rho} + \frac{\mathbf{p}_s}{a(\rho, \rho_s, \eta)} \\ &= \frac{\rho \nabla \phi + \gamma \nabla \lambda + \rho_s \nabla \eta + \gamma_s \nabla \lambda_s}{\rho} + \frac{\rho_s \nabla \eta + \gamma_s \nabla \lambda_s}{a(\rho, \rho_s, \eta)}. \end{aligned} \quad (46)$$

Such equations are less fundamental than the gradient representation of the momenta. They pertain here to the particular model, but, for this model, they are very useful. Along with the Clebsch representations of the thermodynamic intensities, Eqs. (35) and (36), the velocity or momentum representations play an essential role in the theory of the nonequilibrium thermodynamic potentials and Poisson brackets (Secs. IX and X).

The stationary Lagrangian  $\Lambda$  results from the stationarity conditions, Eqs. (33)–(36), as the following functional Legendre transform of the kinetic potential  $L$ :

$$\Lambda = L - \rho \frac{\delta L}{\delta \rho} - \rho_s \frac{\delta L}{\delta \rho_s} \quad (47)$$

and it is equal to a nonequilibrium pressure  $P$  which depends on the transfer velocities, intensities, and phases as its natural variables. For the model using the Onsager potentials

$$\begin{aligned} \Lambda &= \frac{1}{2} \rho \mathbf{u}^2 - \rho e^{\text{eq}}(\rho, \rho_s) - \rho \Psi(x, t) + \frac{1}{2} a(\rho, \rho_s, \eta)(\mathbf{u}_s - \mathbf{u})^2 - \frac{1}{2} b(\rho, \rho_s, \eta)(\nabla \rho_s - \beta \nabla \rho)^2 + \rho_s T^{\text{eq}}(\rho, \rho_s) \\ &\quad - \frac{1}{2} \rho_s \frac{\partial a}{\partial \rho_s} (\mathbf{u}_s - \mathbf{u})^2 + \frac{1}{2} \rho_s \frac{\partial b}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho)^2 - \rho_s b \frac{\partial \beta}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho - \rho_s \nabla \cdot [\eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)] \\ &\quad + \rho \mu^{\text{eq}}(\rho, \rho_s) + \rho \Psi(x, t) - \frac{1}{2} \rho \mathbf{u}^2 - \frac{1}{2} \rho \frac{\partial a}{\partial \rho} (\mathbf{u}_s - \mathbf{u})^2 + \frac{1}{2} \rho \frac{\partial b}{\partial \rho} (\nabla \rho_s - \beta \nabla \rho)^2 - \rho b \frac{\partial \beta}{\partial \rho} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho \\ &\quad + \rho \nabla \cdot [\eta D_s c_v^{-1} \beta (\nabla \rho_s - \beta \nabla \rho)], \end{aligned} \quad (48)$$

where  $a$  and  $b$  are defined by Eqs. (39) and (40). This yields

$$\begin{aligned} \Lambda &= P(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \eta) \\ &= P^{\text{eq}}(\rho, \rho_s) + \frac{1}{2} a^*(\rho, \rho_s, \eta)(\mathbf{u}_s - \mathbf{u})^2 - \frac{1}{2} b^*(\rho, \rho_s, \eta)(\nabla \rho_s - \beta \nabla \rho)^2 - \left[ \rho_s b \frac{\partial \beta}{\partial \rho_s} + \rho b \frac{\partial \beta}{\partial \rho} \right] (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho \\ &\quad - \rho_s \nabla \cdot [\eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)] + \rho \nabla \cdot [\eta D_s c_v^{-1} \beta (\nabla \rho_s - \beta \nabla \rho)], \end{aligned} \quad (49)$$



where  $a^*$  and  $b^*$  are the Legendre transforms of  $a$  and  $b$  with respect to densities  $\rho_s$  and  $\rho$ . The nonequilibrium (second and further lines) contributions to the pressure are related to the effects of the second viscosity.

#### IV. NÖTHER'S ENERGY FOR FLUID WITH HEAT

The total energy density  $E$  computed as the component  $G^{44}$  of the energy-momentum tensor  $G^{ik}$  is

$$\begin{aligned} E = G^{44} &= \sum_l \frac{\partial q_l}{\partial \bar{x}_4} \frac{\partial \Lambda}{\partial (\partial q_l / \partial \bar{x}_4)} - \Lambda \\ &= \sum_l \frac{\partial q_l}{\partial t} \frac{\partial \Lambda}{\partial (\partial q_l / \partial t)} - \Lambda. \end{aligned} \quad (50)$$

$$\begin{aligned} E &= [\rho \mathbf{u} - a(\mathbf{u}_s - \mathbf{u})] \cdot \mathbf{u} + a(\mathbf{u}_s - \mathbf{u}) \cdot \mathbf{u}_s - L \\ &= \rho \mathbf{u}^2 + a(\mathbf{u}_s - \mathbf{u})^2 - L \\ &= -\eta \frac{1}{2} \kappa^{-1} (\rho, \rho_s) \rho_s^2 (\mathbf{u}_s - \mathbf{u})^2 + \frac{1}{2} \eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)^2 + \frac{1}{2} \rho \mathbf{u}^2 + \frac{1}{2} \rho^{-1} \mathbf{g} \mathbf{g}^2 + \rho e^{\text{eq}}(\rho, \rho_s) + \rho \Psi(x, t). \end{aligned} \quad (53)$$

This can be written as follows:

$$E = \frac{1}{2} \rho \mathbf{u}^2 + \frac{1}{2} \rho^{-1} \mathbf{g} \mathbf{g}^2 + \rho e^{\text{eq}}(\rho, \rho_s) + \rho \Psi(x, t) - \eta (\Phi - \Psi), \quad (54)$$

where the difference  $\Phi - \Psi$  represents the co-called thermodynamic Hamiltonian [21]. Thus the total energy density is equal to that obtained in nonequilibrium statistical mechanics [2,18] with accuracy to the phase ( $\eta$ ) term containing Onsager's thermodynamic Hamiltonian.

If the evolution equation for the entropy flux is such that  $\Phi - \Psi$  vanishes (Onsagerian property) the total energy density  $E$  coincides numerically with that of nonequilibrium statistical mechanics. The evolution obeying  $\Phi = \Psi$  is generally a rough approximation of the motion and holds only very close to equilibrium. Far from equilibrium the formula (54) should hold in its entirety, and the qualitative and quantitative role of the  $\eta$  term cannot be excluded, provided, of course, that the process model based on the dissipation function is still acceptable.

Three crucial points should be kept in mind.

$$\begin{aligned} E(\rho, \rho_s, \mathbf{p}, \mathbf{p}_s, \eta, \mathbf{x}, t) &= \frac{1}{2} \rho^{-1} \mathbf{p}^2 + \rho^{-1} \mathbf{p} \cdot \mathbf{p}_s + \frac{1}{2} \rho^{-1} \left\langle 1 + \frac{\rho}{\rho_s^2 (\rho^{-1} \mathbf{g} - \eta \kappa^{-1})} \right\rangle \mathbf{p}_s^2 \\ &+ \eta \Psi(\rho, \rho_s, \nabla \rho_s, \nabla \rho) + \rho e^{\text{eq}}(\rho, \rho_s) + \rho \Psi(x, t), \end{aligned} \quad (55)$$

where the dissipation potential  $\Psi$  is given by Eq. (28). This is the fundamental equation, in the sense of Callen [16], for the single-component nonequilibrium fluid conducting heat. We show here that it contains all the information about both statics and dynamics of the fluid. Such equations are known in thermostatics, where they operate only with standard thermodynamic variables (here  $\rho$  and  $\rho_s$ ), or in the reversible fluid dynamics

For arbitrary  $L$  of Eq. (19) or (30)

$$\begin{aligned} E &= \frac{\partial \Lambda}{\partial (\partial \phi / \partial t)} \frac{\partial \phi}{\partial t} + \frac{\partial \Lambda}{\partial (\partial \eta / \partial t)} \frac{\partial \eta}{\partial t} + \frac{\partial \Lambda}{\partial (\partial \lambda / \partial t)} \frac{\partial \lambda}{\partial t} \\ &+ \frac{\partial \Lambda}{\partial (\partial \lambda_s / \partial t)} \frac{\partial \lambda_s}{\partial t} - \Lambda \\ &= (\rho \nabla \phi + \gamma \nabla \lambda) \cdot \mathbf{u} + (\rho_s \nabla \eta + \gamma_s \nabla \lambda_s) \cdot \mathbf{u}_s - L \end{aligned} \quad (51)$$

and in view of the gradient representations of the momenta, Eqs. (43) and (44)

$$E = \mathbf{p} \cdot \mathbf{u} + \mathbf{p}_s \cdot \mathbf{u}_s - L. \quad (52)$$

This is a generalization of the well-known formula for energy of classical mechanics  $E = \mathbf{p} \cdot \mathbf{u} - L$  including thermal degrees of freedom. For  $L$  of Eqs. (22) and (30),

(1) For any proper description of motion the energy  $E$  should be expressed in terms of the momenta rather than the velocities or fluxes.

(2) The transfer implied by  $E^{\text{class}}$  is reversible whereas that implied by  $E$  is not, even if numerically,  $\Phi = \Psi$ .

(3) Far from equilibrium, formula (54) should hold in its entirety, and deviation from  $E^{\text{class}}$  (due to the thermal phase  $\eta$ ) cannot be excluded.

Hence the basic conclusion follows: One may have  $E = (\text{numerically}) E^{\text{class}}$  which contains more information than  $E^{\text{class}}$ , thus leading to irreversible equations of transport. We will show superiority of  $E$  over  $E^{\text{class}}$ .

#### V. FUNDAMENTAL EQUATION AND THE ENERGY-MOMENTUM TENSOR

The natural variables of energy are momenta, not velocities or fluxes. Therefore Eq. (54) should be expressed in terms of  $\mathbf{p}$  and  $\mathbf{p}_s$ . Since  $\mathbf{u}_s - \mathbf{u} = \mathbf{p}_s / a$  and  $\mathbf{u} = (\mathbf{p} + \mathbf{p}_s) / \rho$  the energy density  $E$  of the fluid with heat becomes

[2,3,22,23].

An essential difference of the present equation from other equations of this sort is that it contains explicitly the new variable thermal phase  $\eta$ , which preserves the irreversibility property. While it has recently been predicted that the explicit phase  $\eta$  in  $E$  means that irreversibility is built in [4], no examples have been presented until now, to the authors' knowledge. This also means that a

characteristic set of ordinary differential equations (corresponding to motions under gradients of  $E$ ) is non-Hamiltonian; however, we omit here the discussion of this important point.

Differentiating  $E$  with respect to  $\eta$  yields the entropy generation

$$\begin{aligned} \frac{\partial E}{\partial \eta} &= \frac{\rho_s^2 \kappa^{-1} \mathbf{p}_s^2}{2[\rho_s^2(\rho^{-1}g - \eta\kappa^{-1})]^2} + \Psi(\rho, \rho_s, \nabla\rho_s, \nabla\rho) \\ &= \frac{1}{2}\rho_s^2 \kappa^{-1}(\mathbf{u}_s - \mathbf{u})^2 + \Psi(\rho, \rho_s, \nabla\rho_s, \nabla\rho) = \Phi + \Psi. \end{aligned} \quad (56)$$

The derivatives of  $E$  with respect to momenta  $\mathbf{p}$  and  $\mathbf{p}_s$  are the absolute transfer velocities of matter and entropy

$$\frac{\partial E}{\partial \mathbf{p}} = \frac{\mathbf{p} + \mathbf{p}_s}{\rho} = \mathbf{u} = \frac{\mathbf{J}}{\rho}, \quad (57)$$

$$\frac{\partial E}{\partial \mathbf{p}_s} = \frac{\mathbf{p}}{\rho} + \mathbf{p}_s \left[ \frac{1}{\rho} + \frac{1}{a} \right] = \mathbf{u}_s = \frac{\mathbf{J}_s}{\rho_s}. \quad (58)$$

The negative partial derivatives of  $E$  with respect to space coordinates (independent variables) are the external force density  $\rho\mathbf{F}$ ,

$$\frac{\partial E}{\partial \mathbf{x}} = \rho \nabla \Psi = -\rho \mathbf{F}. \quad (59)$$

Those with respect to the time  $t$  characterize the energy change in terms of the nonstationarity of the external fields

$$\frac{\partial E}{\partial t} = -\frac{\partial L}{\partial t} = \rho \frac{\partial \Psi}{\partial t}. \quad (60)$$

The energy  $E$  is constant in any system if the external fields are time independent (see also conservation laws, Sec. VIII). This solves the paradox when dissipative systems are sometimes regarded as nonconservative [24], whereas they are actually always conservative when only the external fields are time independent. This also proves that the thermal phase  $\eta$ , not time  $t$ , is the relevant quantity to describe dissipation.

The functional derivatives of the energy  $E$  with respect to the densities must always be taken whenever  $E$  contains the gradients and/or time derivatives of the densities. This gives rise to the nonequilibrium temperatures and chemical potentials

$$T = \frac{\delta E}{\delta \rho_s}, \quad (61)$$

$$\mu = \frac{\delta E}{\delta \rho}. \quad (62)$$

For the Onsager model of dissipation, from Eq. (55),

$$\begin{aligned} \frac{\delta E}{\delta \rho_s} &\equiv \frac{\partial E}{\partial \rho_s} - \nabla \cdot \frac{\partial E}{\partial \nabla \rho_s} \\ &= T^{\text{eq}}(\rho, \rho_s) + \frac{1\partial a^{-1}}{2\partial \rho_s} \mathbf{p}_s^2 + \frac{1\partial b}{2\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho)^2 - b \frac{\partial \beta}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho - \nabla \cdot [\eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)] \\ &= T^{\text{eq}}(\rho, \rho_s) - \frac{1\partial a}{2\partial \rho_s} \left[ \frac{\mathbf{p}}{a} \right]^2 + \frac{1\partial b}{2\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho)^2 - b \frac{\partial \beta}{\partial \rho_s} (\nabla \rho_s - \beta \nabla \rho) \cdot \nabla \rho - \nabla \cdot [\eta D_s c_v^{-1} (\nabla \rho_s - \beta \nabla \rho)] \\ &= -\frac{\delta L}{\delta \rho_s} = T(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \eta) \end{aligned} \quad (63)$$

coincidence with Eq. (37) is achieved since  $\mathbf{p}_s/a = \mathbf{u}_s - \mathbf{u}$ . Similarly

$$\begin{aligned} \frac{\delta E}{\delta \rho} &\equiv \frac{\partial E}{\partial \rho} - \nabla \cdot \frac{\partial E}{\partial \nabla \rho} \\ &= -\frac{\delta L}{\delta \rho} \equiv -\left[ \frac{\partial L}{\partial \rho} - \nabla \cdot \frac{\partial L}{\partial \nabla \rho} \right] = \mu(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \eta), \end{aligned} \quad (64)$$

where  $\mu$  is given by Eq. (38). This result and Eq. (47) prove that the theory of nonequilibrium thermodynamic

potentials (which are actually the functionals rather than the potentials in the classical sense) should be based on the Legendre transformations involving the functional rather than the ordinary partial derivatives.

## VI. DYNAMICS THROUGH FUNDAMENTAL EQUATION I— HAMILTONIAN

When the gradient representations of the momenta, Eqs. (43) and (44), are substituted into  $E$ , Eq. (55), the following Hamiltonian density is obtained:

$$\begin{aligned} H(\rho, \rho_s, \nabla \rho, \nabla \rho_s, \nabla \phi, \nabla \eta, \phi, \eta, \nabla \lambda, \nabla \lambda_s, \gamma, \gamma_s, \mathbf{x}, t) &= \frac{1}{2}\rho^{-1}(\rho \nabla \phi + \gamma \nabla \lambda)^2 + \rho^{-1}(\rho \nabla \phi + \gamma \nabla \lambda) \cdot (\rho_s \nabla \eta + \gamma_s \nabla \lambda_s) \\ &\quad + \frac{1}{2}\rho^{-1} \left\langle 1 + \frac{\rho}{\rho_s^2(\rho^{-1}g - \eta\kappa^{-1})} \right\rangle (\rho_s \nabla \eta + \gamma_s \nabla \lambda_s)^2 \\ &\quad + \eta \Psi(\rho, \rho_s, \nabla \rho, \nabla \rho_s) + \rho e^{\text{eq}}(\rho, \rho_s) + \rho \Psi(\mathbf{x}, t), \end{aligned} \quad (65)$$

which allows one to describe all dynamics of the problem in terms of the Poisson brackets formalism (see Sec. X). The matter phase  $\phi$  is not explicitly present in  $H$  and  $E$  since there are no chemical reactions in the system; otherwise the phase  $\phi_i$  of the individual species would inevitably appear [14].

In terms of  $H$ , the action functional has the general structure of Hamilton-Jacobi type,

$$A = - \int_{t_1}^{t_2} \left[ H(\rho, \rho_s \nabla \rho, \nabla \rho_s, \rho \nabla \phi + \gamma \nabla \lambda, \rho_s \nabla \eta + \gamma_s \nabla \lambda_s, \eta, \phi, \mathbf{x}, t) + \rho_s \frac{\partial \eta}{\partial t} + \gamma_s \frac{\partial \lambda_s}{\partial t} + \rho \frac{\partial \phi}{\partial t} + \gamma \frac{\partial \lambda}{\partial t} \right] dV dt. \quad (66)$$

It can immediately be verified that the formal application of Eq. (50) to the integrand  $\Lambda$  of Eq. (66) recovers the energy  $E$  in the form of  $H$ . The integrand  $\Lambda$  is used below to determine other components of the energy-momentum tensor in terms of  $H$  rather than  $\Lambda$  itself. For this purpose the following equalities are helpful, which hold for our heat transfer model:

$$\frac{\partial H}{\partial \nabla \phi} = \mathbf{p} + \mathbf{p}_s = \rho \mathbf{u} \quad (\text{mass flux}), \quad (67)$$

$$\begin{aligned} \frac{\partial H}{\partial \nabla \eta} &= \frac{\rho_s}{\rho} (\mathbf{p} + \mathbf{p}_s) + \frac{\rho_s}{a} \mathbf{p}_s \\ &= \rho_s \mathbf{u} + \rho_s (\mathbf{u}_s - \mathbf{u}) = \rho_s \mathbf{u}_s \quad (\text{entropy flux}), \end{aligned} \quad (68)$$

$$\frac{\partial H}{\partial \nabla \gamma} = \frac{\partial H}{\partial \nabla \gamma_s} = 0, \quad (69)$$

and

$$\frac{\partial H}{\partial \nabla \lambda} = \rho^{-1} \gamma (\mathbf{p} + \mathbf{p}_s) = \rho^{-1} \gamma \rho \mathbf{u} = \gamma \mathbf{u}, \quad (70)$$

$$\begin{aligned} \frac{\partial H}{\partial \nabla \lambda_s} &= \rho^{-1} \gamma_s (\mathbf{p} + \mathbf{p}_s) + \frac{\gamma_s}{a} \mathbf{p}_s \\ &= \gamma_s \mathbf{u} + \gamma_s (\mathbf{u}_s - \mathbf{u}) = \gamma_s \mathbf{u}_s. \end{aligned} \quad (71)$$

The last two equations represent the ‘‘flows of identity’’ for the matter and the entropy. We will use  $H$  for two purposes: (a) obtaining the conservation laws, and (b) representing dynamics in canonical form.

For the purpose of conservation laws the knowledge of all the components of the energy-moment tensor  $G^{ik}$  are necessary. We know already only the energy density, Eq. (54) or (55). Now we will find other components. According to Eq. (4) the spatial part of  $G^{ik}$  or the stress tensor  $T^{\alpha\beta} = G^{\alpha\beta}$  ( $\alpha, \beta = 1, 2, 3$ ) is

$$T^{\alpha\beta} = \sum_l \frac{\partial q_l}{\partial x^\alpha} \left[ \frac{\partial \Lambda}{\partial (\partial q_l / \partial x^\beta)} \right] - \delta^{\alpha\beta} \Lambda. \quad (72)$$

From Eqs. (66) and (72) and the gradient representations of momenta, Eqs. (43) and (44), for arbitrary  $H$  and  $L$

$$\begin{aligned} T^{\alpha\beta} &= \frac{\partial \phi}{\partial x^\alpha} \frac{-\partial H}{\partial (\partial \phi / \partial x^\beta)} + \frac{\partial \eta}{\partial x^\alpha} \frac{-\partial H}{\partial (\partial \eta / \partial x^\beta)} + \frac{\partial \lambda}{\partial x^\alpha} \frac{-\partial H}{\partial (\partial \lambda / \partial x^\beta)} + \frac{\partial \lambda_s}{\partial x^\alpha} \frac{-\partial H}{\partial (\partial \lambda_s / \partial x^\beta)} - \delta^{\alpha\beta} P \\ &= - \left[ \rho \frac{\partial \phi}{\partial x^\alpha} + \gamma \frac{\partial \lambda}{\partial x^\alpha} \right] u^\beta - \left[ \rho_s \frac{\partial \eta}{\partial x^\alpha} + \gamma_s \frac{\partial \lambda_s}{\partial x^\alpha} \right] u_s^\beta - \delta^{\alpha\beta} P \\ &= - \frac{\partial L}{\partial u^\alpha} u^\beta - \frac{\partial L}{\partial u_s^\alpha} u_s^\beta - \delta^{\alpha\beta} P \end{aligned} \quad (73)$$

and for Onsager’s model of heat transfer

$$\begin{aligned} T^{\alpha\beta} &= -p^\alpha u^\beta - p_s^\alpha u_s^\beta - \delta^{\alpha\beta} P \\ &= -\rho u^\alpha u^\beta + a (u_s - u)^\alpha u^\beta - a (u_s - u)^\alpha u_s^\beta - \delta^{\alpha\beta} P \\ &= -\rho u^\alpha u^\beta - a(\rho_s, \rho, \eta) (u_s - u)^\alpha (u_s - u)^\beta \\ &\quad - \delta^{\alpha\beta} P(\rho_s, \rho, \nabla \rho_s, \nabla \rho, \eta), \end{aligned} \quad (74)$$

where  $a(\rho_s, \rho, \eta)$  is defined by Eq. (39) and  $P(\rho_s, \rho, \text{grad} \rho_s, \text{grad} \rho, \eta)$  is the nonequilibrium pressure given by Eq. (49). Entropy and heat flows are therefore inherently connected with nonequilibrium stresses, represented here by the middle term in the second line of Eq. (74). This was first revealed by Grad [17] in his mo-

ment analysis of the solution of the Boltzmann equation. The nonequilibrium pressure tensor related to the viscous stresses is

$$\Pi^{\alpha\beta} = a(\rho_s, \rho, \eta) (u_s - u)^\alpha (u_s - u)^\beta. \quad (75)$$

It vanishes at equilibrium when  $\mathbf{u}_s = \mathbf{u}$ . It should be realized that this is the defining macroscopic expression for the viscous stress, which is not linked to any phenomenological law relating this stress to the velocity gradients. (A similar remark holds for the heat flux, discussed below.) The deviatoric and spherical parts of these stresses can be evaluated in the usual way [9]. Also the  $P$  term can be split into equilibrium and nonequilibrium parts, Eq. (49), giving rise to the bulk viscosity effects.

The momentum density  $-\Gamma^\alpha = -G^{\alpha 4}$  is

$$\begin{aligned}\Gamma^\alpha &= -G^{\alpha 4} = -\sum_I \frac{\partial q_I}{\partial x^\alpha} \frac{\partial \Lambda}{\partial (\partial q_I / \partial t)} \\ &= -\sum_I \frac{\partial \Lambda}{\partial (\partial q_I / \partial t)} (\nabla q_I)^\alpha\end{aligned}\quad (76)$$

yielding, in vector notation for  $\Lambda$  of Eq. (66),

$$\begin{aligned}\Gamma &= -\frac{\partial \Lambda}{\partial (\partial \phi / \partial t)} \nabla \phi - \frac{\partial \Lambda}{\partial (\partial \eta / \partial t)} \nabla \eta - \frac{\partial \Lambda}{\partial (\partial \lambda / \partial t)} \nabla \lambda \\ &\quad - \frac{\partial \Lambda}{\partial (\partial \lambda_s / \partial t)} \nabla \lambda_s \\ &= \rho \nabla \phi + \gamma \nabla \lambda + \rho_s \nabla \eta + \gamma_s \nabla \lambda_s = \frac{\partial L}{\partial \mathbf{u}} + \frac{\partial L}{\partial \mathbf{u}_s}\end{aligned}\quad (77)$$

for arbitrary  $L$ . In our model,

$$\Gamma = \mathbf{p} + \mathbf{p}_s = \rho \mathbf{u} \quad (78)$$

so the classical result holds that the momentum density is the mass flow.

The energy flux density  $Q^\beta = -G^{4\beta}$  is

$$Q^\beta = G^{4\beta} = \sum_I \frac{\partial q_I}{\partial t} \frac{\partial \Lambda}{\partial (\partial q_I / \partial x^\beta)} = \sum_I \frac{\partial \Lambda}{\partial (\nabla q_I)^\beta} \frac{\partial q_I}{\partial t} \quad (79)$$

and hence

$$\begin{aligned}Q &= -\frac{\partial H}{\partial (\nabla \phi)} \frac{\partial \phi}{\partial t} - \frac{\partial H}{\partial (\nabla \lambda)} \frac{\partial \lambda}{\partial t} \\ &\quad - \frac{\partial H}{\partial (\nabla \eta)} \frac{\partial \eta}{\partial t} - \frac{\partial H}{\partial (\nabla \lambda_s)} \frac{\partial \lambda_s}{\partial t} \\ &= -\rho \mathbf{u} \frac{\partial \phi}{\partial t} - \gamma \mathbf{u} \frac{\partial \lambda}{\partial t} - \rho_s \mathbf{u}_s \frac{\partial \eta}{\partial t} - \gamma_s \mathbf{u}_s \frac{\partial \lambda_s}{\partial t}.\end{aligned}\quad (80)$$

From this it is seen that, in order to get  $Q$ , the partial time derivatives of the multipliers should be eliminated. These will be expressed first in terms of their gradients and then the gradient representation of the momenta will be exploited. We substitute into Eq. (80) the already known stationarity conditions

$$\frac{\partial \eta}{\partial t} = -\mathbf{u}_s \cdot \nabla \eta + \frac{\delta L}{\delta \rho_s} = -\mathbf{u}_s \cdot \nabla \eta - T, \quad (81)$$

$$\frac{\partial \lambda_s}{\partial t} = -\mathbf{u}_s \cdot \nabla \lambda, \quad (82)$$

$$\frac{\partial \phi}{\partial t} = -\mathbf{u} \cdot \nabla \phi - \frac{\delta L}{\delta \rho} = -\mathbf{u} \cdot \nabla \phi - \mu, \quad (83)$$

and

$$\frac{\partial \lambda}{\partial t} = -\mathbf{u} \cdot \nabla \lambda, \quad (84)$$

which yields in terms of  $L$

$$\begin{aligned}Q &= \rho \mathbf{u} \left[ \mathbf{u} \cdot \nabla \phi - \frac{\delta L}{\delta \rho} \right] + \gamma \mathbf{u} (\mathbf{u} \cdot \nabla \lambda) + \rho_s \mathbf{u}_s \left[ \mathbf{u} \cdot \nabla \eta - \frac{\delta L}{\delta \rho_s} \right] + \gamma_s \mathbf{u}_s (\mathbf{u}_s \cdot \nabla \lambda_s) \\ &= -\rho \mathbf{u} \frac{\delta L}{\delta \rho} - \rho_s \mathbf{u}_s \frac{\delta L}{\delta \rho_s} + \mathbf{u} [\mathbf{u} \cdot (\rho \nabla \phi + \gamma \nabla \lambda)] + \mathbf{u}_s [\mathbf{u}_s \cdot (\rho_s \nabla \eta + \gamma_s \nabla \lambda_s)] \\ &= \mathbf{u} \left[ \mathbf{u} \cdot \frac{\partial L}{\partial \mathbf{u}} - \rho \frac{\delta L}{\delta \rho} \right] + \mathbf{u}_s \left[ \mathbf{u}_s \cdot \frac{\partial L}{\partial \mathbf{u}_s} - \rho_s \frac{\delta L}{\delta \rho_s} \right].\end{aligned}\quad (85)$$

In terms of the physical quantities

$$\begin{aligned}Q &= \mathbf{u} (\mathbf{p} \cdot \mathbf{u} + \rho \mu) + \mathbf{u}_s (\mathbf{p}_s \cdot \mathbf{u}_s + \rho_s T) \\ &= \mathbf{u} (\mu \rho + T \rho_s) + u^2 \mathbf{p} + u_s^2 \mathbf{p}_s + T \rho_s (\mathbf{u}_s - \mathbf{u}) \\ &= \mathbf{u} [\mu \rho + T \rho_s + \rho u^2 + \mathbf{p}_s \cdot (\mathbf{u}_s - \mathbf{u})] - u^2 \mathbf{p}_s - \mathbf{u} \cdot \mathbf{p}_s (\mathbf{u}_s - \mathbf{u}) + u_s^2 \mathbf{p}_s + T \rho_s (\mathbf{u}_s - \mathbf{u}) \\ &= \mathbf{u} (E + P) + \mathbf{u}_s \cdot \mathbf{p}_s (\mathbf{u}_s - \mathbf{u}) + T \rho_s (\mathbf{u}_s - \mathbf{u}) \\ &= \mathbf{u} (E + P) + [a (\mathbf{u}_s - \mathbf{u}) (\mathbf{u}_s - \mathbf{u})] \cdot \mathbf{u}_s + T \rho_s (\mathbf{u}_s - \mathbf{u}) \\ &= \mathbf{u} (E + P) + \Pi \cdot \mathbf{u}_s + \mathbf{j}_q.\end{aligned}\quad (86)$$

In the above equation the following equality has been used:

$$\mu \rho + T \rho_s + \rho u^2 + \mathbf{p}_s \cdot (\mathbf{u}_s - \mathbf{u}) = E + P, \quad (87)$$

which can be verified by straightforward but lengthy calculus using the expressions for nonequilibrium  $\mu$ ,  $T$ ,  $P$ , and  $E$ . It is a nonequilibrium extension of the well-known static formula

$$\mu^{\text{eq}} \rho + T^{\text{eq}} \rho_s = \rho e^{\text{eq}} + P^{\text{eq}}. \quad (88)$$

Equation (87) without the dissipation potentials  $\Phi$  and  $\Psi$  and the thermal phase  $\eta$  (contained therein implicitly) can be derived in reversible extended thermodynamics of a fluid with heat flow; see Eq. (38) in Ref. [3].

In Eq. (86) the work of the nonequilibrium thermal stresses,  $\Pi \cdot \mathbf{u}_s$ , appears. It is related to the entropy veloc-

ity rather than to that of matter. Since the role of the velocity gradients has been ignored the viscosity effects represented by  $\Pi$  in the model are associated only with the flow of the entropy and heat, excluding that of the matter [17]. It is practical to split this work into two parts, the convective work of the nonequilibrium stresses,  $\Pi \cdot \mathbf{u}$ , and their diffusional work  $\Pi \cdot (\mathbf{u}_s - \mathbf{u})$ .

### VII. MACROSCOPIC VIEW OF HEAT AND EQUATIONS OF HEAT TRANSFER

In the energy flux  $\mathbf{Q}$  the "pure heat flux" (excluding any contribution of stresses  $\Pi$ ) appears,

$$\mathbf{j}_q = T\rho_s(\mathbf{u}_s - \mathbf{u}) = T\mathbf{j}_s. \quad (89)$$

As in the case of the nonequilibrium stresses it should be realized that this is a defining macroscopic expression for the heat flux which does not have anything in common with any phenomenological law linking that flux with the temperature gradient. An equation describing that link in this formalism is contained in the equations of motion, the stationarity conditions of the action functional, Eqs. (35)–(40), (43), and (44). This may be verified by transforming these equations into an equation directly describing the heat flow  $\mathbf{j}_q$ , Eq. (89). A transformation procedure for an arbitrary kinetic potential  $L$  is given elsewhere [14], and since it resembles that known in the theory of perfect fluids, known as the method of eliminating the Lagrange multipliers [25] it is omitted here. Only the ready-to-use result is given below:

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \frac{\partial L}{\rho_s \partial \mathbf{u}_s} \right] + \nabla \cdot \left[ \frac{\partial L}{\rho_s \partial \mathbf{u}_s} \cdot \mathbf{u}_s - \frac{\delta L}{\delta \rho_s} \right] \\ - \mathbf{u}_s \times \left[ \nabla \times \frac{\partial L}{\rho_s \partial \mathbf{u}_s} \right] + \frac{\sigma_s}{\rho_s} \left[ \frac{\partial L}{\rho_s \partial \mathbf{u}_s} - \nabla \eta \right] = 0. \end{aligned} \quad (90)$$

As follows from the results of Sec. IX the so-called "hotter" temperatures  $T^+$ , Eq. (112), and the thermal momenta per unit entropy, Eq. (106), play the essential role in this equation. However, we work below in terms of  $T$  rather than  $T^+$ . For  $L$  of Eq. (22), Eq. (90) yields

$$\begin{aligned} \mathbf{j}_q = T\mathbf{j}_s \equiv T\rho_s(\mathbf{u}_s - \mathbf{u}) &= \frac{T\rho_s \mathbf{p}_s}{a} = \frac{T\rho_s^2 \mathbf{i}_s}{a} \\ &= \frac{T\rho_s^2 \mathbf{i}_s}{\rho_s^2(\rho^{-1}g - \kappa^{-1}\eta)} = \frac{T\mathbf{i}_s}{\rho^{-1}g - \kappa^{-1}\eta} = \frac{T\mathbf{i}_s}{\kappa^{-1}T\tau - \kappa^{-1}\eta} = \frac{T\kappa}{\tau T - \eta} \mathbf{i}_s, \end{aligned} \quad (96)$$

where Eq. (12) expressing  $g$  in terms of the heat relaxation time  $\tau$  has been used. [Equation (96) gives already described relation  $\mathbf{j}_q = \kappa \mathbf{i}_s / \tau$  in a classical limit when the effect of  $\eta$  is ignorable.] Multiplying Eq. (91) by the coefficient of  $\mathbf{i}_s$  in Eq. (96) and rearranging, one obtains

$$\kappa \left[ \frac{\partial}{\partial t} \left[ \frac{(\tau T - \eta) \mathbf{j}_q}{T\kappa} \right] + \nabla \cdot \left[ \frac{(\tau T - \eta) \mathbf{j}_q \cdot \mathbf{u}_s}{T\kappa} \right] - \mathbf{u}_s \times \left[ \nabla \times \frac{(\tau T - \eta) \mathbf{j}_q}{T\kappa} \right] - \frac{\nabla \eta}{\tau_s} \right] + \mathbf{j}_q \frac{T(\tau - \tau_s) - \eta}{\tau_s T} + \mathbf{j}_q = -\kappa \nabla T. \quad (97)$$

$$\tau_s \left[ \frac{\partial}{\partial t} \mathbf{i}_s + \nabla \cdot (\mathbf{i}_s \cdot \mathbf{u}_s) - \mathbf{u}_s \times (\nabla \times \mathbf{i}_s) \right] - \nabla \eta + \mathbf{i}_s = -\tau_s \nabla T. \quad (91)$$

This equation allows a nonequilibrium steady state, whereas its reversible counterparts (for the "ideal conductors") do not. It contains odd and even terms with respect to time reversal, which is why it is capable of describing irreversible flows. This is an equation of heat transfer of the Maxwell-Cattaneo structure [26] with the entropic relaxation time  $\tau_s$ ,

$$\tau_s \equiv \frac{\rho_s}{\sigma_s}. \quad (92)$$

Note that the relaxation time was not introduced so far in the action approach so it can be defined now in a suitable way. The most essential property of this equation of motion is associated with its irreversibility. It is caused by the presence of the flux  $\mathbf{i}_s$  itself, not only its time derivative. In corresponding equations of reversible processes fluxes are not explicitly included, and only their time derivatives appear [20]. For weak dissipation and large thermal conductivity  $\kappa$ , it results from Eq. (96) linking  $\mathbf{i}_s$  and  $\mathbf{j}_q$  that  $\mathbf{i}_s = g\rho^{-1} \mathbf{j}_q T^{-1} = \tau\kappa^{-1} \mathbf{j}_q$ , and hence, after linearization,

$$\tau \frac{d}{dt} \mathbf{j}_q + \frac{\tau}{\tau_s} \mathbf{j}_q = -\kappa \nabla T. \quad (93)$$

The Maxwell-Cattaneo equation is obtained for  $\tau = \tau_s$ , the entropy relaxation time identified with that of heat. As is well known, combining this equation with the internal energy balance yields the damped wave equation for the temperature

$$\frac{dT}{dt} = D_s \left[ \nabla^2 T - \frac{d^2 T}{c_0^2 dt^2} \right] \quad (94)$$

preserving causality due to the finite propagation speed of the thermal disturbances

$$c_0 = (D_s / \tau)^{1/2} = [\kappa / (\rho c_p \tau)]^{1/2}. \quad (95)$$

However, one would like better to have a more exact equation for heat flow in terms of the heat flux rather than the momentum  $\mathbf{i}_s$ . Since

Again the correspondence with Fourier's law appears when the entropy relaxation time  $\tau_s$  is the same as that of heat  $\tau = D_s/c_0^2$ , and when the nonclassical terms with  $\eta$  can be ignored. Various equivalent forms of Eq. (97) can be obtained. The simplest structures appear when the total time derivative of the thermal momentum is used. However, we will not write them down here. The relation of such equations to Fourier's law is always approximate, in view of the approximate nature of the Fourier law itself. But an approximation is also contained in Onsager's theory and in the Lagrangian that we have used related to the Onsager potentials. It is an assumption that, in a dissipative process, the form of the energy function is the same as in a reversible process, the assumption which can never be exact in view of the present theory. Therefore, instead of trying to simplify and then test equations such as Eq. (97), an original set of the Euler equations should be tested (a canonical set, Sec. X).

### VIII. THERMAL PHASE AND PHASE-DEPENDENT CONSERVATION LAWS

The form of the components of the energy-momentum tensor is typical of that of real fluids. Indeed, we have obtained the terms usually regarded as irreversible, the nonequilibrium stresses  $\Pi$ , their work,  $\Pi \cdot \mathbf{u}$ , and the conductive fluxes of the heat and entropy,  $\mathbf{j}_q$  and  $\mathbf{j}_s$ . However, it should be realized that the expressions for the components of the energy-momentum tensor are more general than those encountered in standard textbooks; they contain the contributions of the thermal phase  $\eta$  and the state gradients. The price of the suitable formal coincidence is the complexity of the (functional) expressions for the thermodynamic intensities  $T$  and  $\mu$  and momenta  $\mathbf{p}$  and  $\mathbf{p}_s$ . These now depend not only on the densities of the matter and entropy (classical variables) but also on their gradients and the thermal phase  $\eta$ . The latter variable is inevitable to preserve a nonvanishing entropy generation. Writing the static quantities and dissipation potentials explicitly in  $\mathbf{Q}$  one can obtain the energy flux in a more explicit form

$$\mathbf{Q} = \mathbf{u} \left[ \frac{\rho \mathbf{u}^2}{2} + \rho \Psi(x, t) + \rho e^{\text{eq}}(\rho_s, \rho) + \frac{1}{2} \rho g \mathbf{j}_s^2 - \eta(\Phi - \Psi) \right] + [\mathbf{1} P^{\text{eq}} + \mathbf{1} \Delta P(\rho, \rho_s, \mathbf{u} - \mathbf{u}_s, \nabla \rho_s, \eta) + \Pi] \cdot \mathbf{u} + \Pi \cdot (\mathbf{u}_s - \mathbf{u}) + [T^{\text{eq}} + \Delta T(\rho, \rho_s, \mathbf{u} - \mathbf{u}_s, \nabla \rho_s, \eta)] \mathbf{j}_s, \quad (98)$$

where  $\mathbf{1}$  is the unit tensor and the nonequilibrium corrections to  $P^{\text{eq}}$  and  $T^{\text{eq}}$  result from Eqs. (49) and (37). All classical terms of the energy flux [27] can be identified here, together with a few new or relatively unknown terms, such as the  $g$  term of the nonequilibrium internal energy, the dissipative Hamiltonian term  $-\eta(\Phi - \Psi)$ , the diffusional work  $\Pi \cdot (\mathbf{u}_s - \mathbf{u})$ , and the nonequilibrium correction to the temperature,  $\Delta T$ . That the pressure nonequilibrium correction must exist is known from classical fluid thermomechanics [28]. Here, however, this correction is also phase dependent. When an alternative definition of the heat flux density, including the diffusional work  $\Pi \cdot (\mathbf{u}_s - \mathbf{u})$ , is used,

$$\mathbf{q} = \Pi \cdot (\mathbf{u}_s - \mathbf{u}) + T \mathbf{j}_s \quad (99)$$

rather than  $\mathbf{j}_q = T \mathbf{j}_s$ , then the diffusive entropy flux takes on, in terms of  $\Pi$  and  $\mathbf{q}$ , the form

$$\mathbf{j}_s = \frac{\mathbf{q} - \Pi \cdot (\mathbf{u}_s - \mathbf{u})}{T} \quad (100)$$

Such a form appears in the entropy balances of the extended nonequilibrium thermodynamics [19] where, however, the meaning of the coefficient of  $\Pi$  is not explicitly identified with  $\mathbf{u}_s - \mathbf{u}$ .

Taking  $j = \alpha = 1, 2, 3$ , and  $k = 1, 2, 3, 4$ , in the general formula for the balance of the energy and momentum, Eq. (6), one has the momentum balance

$$\sum_{k=1}^4 \frac{\partial G^{jk}}{\partial x^k} + \frac{\partial \Lambda}{\partial x^j} = \sum_{\beta=1}^3 \frac{\partial G^{\alpha\beta}}{\partial x^\beta} + \frac{\partial \Gamma^\alpha}{\partial t} + \frac{\partial \Lambda}{\partial x^\alpha} = 0, \quad (101)$$

whence, for our model

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u} + \mathbf{1} P + \Pi) = \rho \mathbf{F}. \quad (102)$$

Again, this equation is only formally identical with that known from the classical fluid mechanics or irreversible thermodynamics. Actually it is a generalization of the classical result because the nonequilibrium pressure  $P$  and the nonequilibrium stress  $\Pi$  depend explicitly on the thermal phase  $\eta$  and gradients.

Taking  $j = 4$  in the general balance formula, Eq. (6), one obtains for  $\beta = 1, 2, 3$  the general expression for the energy balance

$$\sum_{k=1}^4 \frac{\partial G^{4k}}{\partial x^k} + \frac{\partial \Lambda}{\partial t} = \sum_{\beta=1}^3 \frac{\partial G^{4\beta}}{\partial x^\beta} + \frac{\partial G^{44}}{\partial t} + \frac{\partial \Lambda}{\partial t} = 0, \quad (103)$$

which yields for our model

$$\nabla \cdot [\mathbf{u}(E + P) + \Pi \cdot \mathbf{u} + \mathbf{q}] + \frac{\partial E}{\partial t} = \rho \frac{\partial \Psi}{\partial t}, \quad (104)$$

where the total energy is given by Eq. (54). Integrating this equation over an arbitrary fixed volume of the space one obtains the law of energy conservation in an isolated system if the external fields are stationary or absent. In any nonisolated system the energy change equals the sum of the net input of  $E$  due to flow and the heat and work terms. These conclusions are, of course standard; however, to our knowledge, they are first obtained formally here for an irreversible process, in which the definitions of the Lagrangian and of the components of  $\mathbf{G}^{ik}$  must be extended to preserve the continuity relations for entropy generation. In the context of Nöther's theorem the applications of these conclusions were known until now only for thermodynamically reversible processes conserving the

entropy, such as processes of perfect fluids [15] or heat superconductors [2,3]. A number of trials in the literature attempt to link dissipation with time-dependent Lagrangians; see, for example, the book by Vujanovic and Jones [24] and Ray's critical paper [29]. It should be observed [consider the  $\Lambda$  term of Eq. (103)] that a time-dependent Lagrangian cannot lead to the energy conservation law. The use of the thermal phase  $\eta$  is necessary to secure simultaneous entropy generation and energy conservation in the absence of time-dependent external fields.

### IX. THERMOHYDRODYNAMIC, PHASE-DEPENDENT POTENTIALS: UNION OF HYDROMECHANICS AND THERMODYNAMICS

Functions or functionals that can be obtained from  $L$  or  $E$  through Legendre transformations are called the thermohydrodynamic potentials (THP). Their dependence on velocities or momenta, state gradients, and phases ( $\eta$  and  $\phi$ ), and their dissipative properties make them the extensions of the classical mechanical Lagrangians and usual thermostatic potentials. Here we give just an introduction to this problem.

One may distinguish three types of THP's. Those obtained from the kinetic potential  $L$  by the thermodynamic Legendre transformation of thermodynamic variables (densities, intensities) are called the THP's of the Lagrangian type, or Lagrangians. These THP's always contain velocities. Those obtained from the kinetic potential  $L$  (or another Lagrangian) by mechanical Legendre transformation involving all the velocities are called the THP's of the energy type, because they always contain the momenta, the natural variables of the energy. For example, the pressure function  $P(\mathbf{u}, \mathbf{u}_s, \rho, \rho_s)$  is a Lagrangian-type THP, whereas the grand potential  $\Omega(\mathbf{p}, \mathbf{p}_s, \rho, \rho_s)$ , which coincides with the negative of  $P$  only in the static case when the role of the kinetic terms is inessential, is a THP of the energy type. In the static situation all Lagrangians become the usual thermodynamic potentials with negative sign, and all the energy-type THP's, as well as Lagrangian-type THP's, become the usual THP's.

The third group is composed of mixed structures, containing both velocities and momenta (and any thermodynamic variables). They are called Routhians, *per analogiam* with such mixed structures in classical mechanics [30,31]. From the viewpoint of their sign in Eq. (105) they may behave both like Lagrangians and like energy-type THP's. The sign of any Routhian, for a given set of its natural variables, can be changed; corresponding with the change of sign in Eq. (105). Energy-type Routhians  $R$  yield the entropy source as the partial derivative of  $R$  with respect to the thermal phase with the positive sign; the Lagrangian-type  $R$ —with the negative sign. The Routhian form is especially useful if some but not all of the extensive (coordinate-like) variables do not appear in the Lagrangian [31].

Potentials obtained by Legendre transformation of a THP with respect to phases (leading to sources of the entropy and species as field variables) and the entropy-

representation THP's are not considered here. The sources are, however, implicit in any TH potentials containing an explicit thermal phase.

The entropy production  $\sigma_s$  is always the partial derivative of an arbitrary THP with respect to the thermal phase  $\eta$ :

$$\begin{aligned} \sigma_s &= -\frac{\partial L}{\partial \eta} = -\frac{\partial P}{\partial \eta} = -\frac{\partial \Gamma_L}{\partial \eta} \dots \\ &= \frac{\partial E}{\partial \eta} = \frac{\partial F}{\partial \eta} = \frac{\partial \Gamma}{\partial \eta} = \frac{\partial \Omega}{\partial \eta} \dots = \Phi + \Psi. \end{aligned} \quad (105)$$

In this formula, the partial derivatives pertain, respectively to the Lagrangian, the pressure (the mechanical transform of  $L$  with respect to both  $\rho$  and  $\rho_s$ ), the transform of  $L$  with respect to  $\rho$  only, the energy, the free energy, the transform of  $E$  with respect to  $\rho$  only, and the grand potential. For the energy-type THP the positive sign of the derivatives should be taken to obtain positive  $\sigma_s$ , whereas for the Lagrangian-type THP the sign should be negative. Note, of course, that different natural variables are held constant in each of the partial derivatives appearing in Eq. (105).

The perfect differentials of the thermodynamic potentials ( $L, P, \Gamma_L, E, F, \Gamma, \Omega$ , etc.) obey formulas generalizing those known for the reversible (sourceless) processes. This means that the generalized momentum densities, Eqs. (43) and (44), can be obtained not only from  $L$  but also from any other THP's containing transfer velocities among their independent variables, which have to be their natural variables. These are the Lagrangian-type THP's. It is sometimes convenient, e.g., in the case of phenomenological equations, to refer these momenta to the units of entropies and masses as the basic entities of the action formalism:

$$\mathbf{i}_s = \rho_s^{-1} \mathbf{p}_s = \frac{\partial L}{\rho_s \partial \mathbf{u}_s} = \frac{\partial P}{\rho_s \partial \mathbf{u}_s} = \frac{\partial \Gamma_L}{\rho_s \partial \mathbf{u}_s} \dots = \nabla \eta + \alpha_s \nabla \lambda_s, \quad (106)$$

$$\mathbf{i} = \rho^{-1} \mathbf{p} = \frac{\partial L}{\rho \partial \mathbf{u}} = \frac{\partial P}{\rho \partial \mathbf{u}} = \frac{\partial \Gamma_L}{\rho \partial \mathbf{u}} \dots = \nabla \phi + \alpha \nabla \lambda. \quad (107)$$

On the other hand, differentiation of the energy-type THP's yields the absolute velocities  $\mathbf{u}$  and  $\mathbf{u}_s$ ,

$$\mathbf{u}_s = \frac{\partial E}{\partial \mathbf{p}_s} = \frac{\partial F}{\partial \mathbf{p}_s} = \dots = \frac{\partial \Gamma}{\partial \mathbf{p}_s} \quad (108)$$

and

$$\mathbf{u} = \frac{\partial E}{\partial \mathbf{p}} = \frac{\partial F}{\partial \mathbf{p}} = \dots = \frac{\partial \Gamma}{\partial \mathbf{p}}, \quad (109)$$

which may also be given gradient representations. Similarly, any of the thermodynamic intensities can be expressed as the derivative of the arbitrary thermodynamic potential involving the corresponding density:

$$T = -\frac{\delta L}{\delta \rho_s} = -\frac{\delta \Gamma_L}{\delta \rho_s} \dots = \frac{\delta E}{\delta \rho_s} = \frac{\delta \Gamma}{\delta \rho_s} = \dots, \quad (110)$$

$$\mu = -\frac{\delta L}{\delta \rho} = \frac{\delta F_L}{\delta \rho} \dots \frac{\delta E}{\delta \rho} = \frac{\delta F}{\delta \rho} = \dots \quad (111)$$

These “cooler” intensities (containing kinetic terms with negative signs) are the most fundamental ingredients of the canonical formalism. It may be shown [4] that the relativistic temperatures of Einstein belong to this category. However, they are certain “differential measures” of the partial (negative) Lagrangians rather than the energies of the flowing elements. There also exist corresponding “differential energies” (identical with Ott’s temperatures [32] in the relativistic case). They appear explicitly in the energy flux formula, Eq. (85), in its original form resulting from the energy-momentum tensor, Eq. (4). The “hotter” intensities are defined on the basis of Eqs. (81)–(85), (106), and (107) as

$$T^+ \equiv \mathbf{i}_s \cdot \mathbf{u}_s + T = \frac{\partial L}{\rho_s \partial \mathbf{u}_s} \cdot \mathbf{u}_s - \frac{\delta L}{\delta \rho_s} = - \left[ \frac{\partial \eta}{\partial t} + \alpha_s \frac{\partial \lambda_s}{\partial t} \right], \quad (112)$$

$$\mu^+ \equiv \mathbf{i} \cdot \mathbf{u} + \mu = \frac{\partial L}{\rho \partial \mathbf{u}} \cdot \mathbf{u} - \frac{\delta L}{\delta \rho} = - \left[ \frac{\partial \phi}{\partial t} + \alpha \frac{\partial \lambda}{\partial t} \right], \quad (113)$$

where the last terms describe their multiplier representation. [Note that the functional derivatives of the Hamiltonian  $H$  are neither cooler nor hotter intensities; see the canonical Eqs. (129)–(136).] In terms of hotter quantities the energy flux (85) takes the simple form

$$\mathbf{Q} = \mathbf{u} \rho \mu^+ + \mathbf{u}_s \rho_s T^+ \quad (114)$$

without division into the “irreversible” and convective terms of the conventional representation, Eq. (86). The quantities  $T^+$  and  $\mu^+$  obey

$$\rho \mu^+ + \rho_s T^+ = E + P, \quad (115)$$

which can be written in terms of  $\mu$  and  $T$  as

$$\rho \mu + \rho_s T + \mathbf{p} \cdot \mathbf{u} + \mathbf{p}_s \cdot \mathbf{u}_s = E + P \quad (116)$$

extending the classical Eq. (88); it is equivalent to Eq. (87). The form (114) stresses that the energy flow is the result of the transfer of the entropy and matter moving with their absolute velocities  $\mathbf{u}_s$  and  $\mathbf{u}$  and all resulting effects are consequences of this fact.

The THP’s have a dynamical role. The theory developed in this work can be recovered without loss in the generality if the Lagrangian  $L$  of the general action functional

$$A = \int \left[ L(\mathbf{u}, \mathbf{u}_s, \rho, \rho_s, \nabla \rho, \nabla \rho_s, \eta, \mathbf{x}, t) - \rho \left[ \frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi \right] - \rho_s \left[ \frac{\partial \eta}{\partial t} + \mathbf{u}_s \cdot \nabla \eta \right] - \gamma \left[ \frac{\partial \lambda}{\partial t} + \mathbf{u} \cdot \nabla \lambda \right] - \gamma_s \left[ \frac{\partial \lambda_s}{\partial t} + \mathbf{u}_s \cdot \nabla \lambda_s \right] \right] dV dt \quad (30')$$

[see Eqs. (19) or (30)] is expressed as the appropriate Legendre transformation of any chosen thermohydrodynamic potential. This THP should be given in terms of its own natural variables. Here the THP’s are discussed in the context of their role in the action functional (30) or (30’). While they can live their independent life, the representations of  $L$  and  $\Lambda$  given below [Eqs. (117)–(122) and (125)–(128)] must be considered jointly with the above-mentioned functional.

An interesting issue is that the thermodynamic variables and their conjugates can be varied independently or jointly in various representations of  $\Lambda$ . Hence there are two classes of the Lagrangians  $\Lambda$ , nonextremal or extremal with respect to the thermodynamic conjugates of the natural variables of a given THP. The former contain these conjugates as independent variables; the latter have them already eliminated and only the natural variables are present. This resembles a situation in mechanics where, as commonly known, the momenta and velocities can be varied independently in the “nonextremal”  $L = \mathbf{p} \cdot d\mathbf{x}/dt - E(\mathbf{p}, \mathbf{x}, t)$  giving rise to Hamilton’s equations of motion. However, one can first substitute the momentum  $\mathbf{p}(d\mathbf{x}/dt, \mathbf{x}, t)$ , found from the extremum condition of such  $L$  with respect to  $\mathbf{p}$ ,  $d\mathbf{x}/dt = \partial E / \partial \mathbf{p}$ , into the expression  $\mathbf{p} \cdot d\mathbf{x}/dt - E(\mathbf{p}, \mathbf{x}, t)$ . Then one works with  $L(d\mathbf{x}/dt, \mathbf{x}, t)$ , in the Lagrangian picture. The two pictures are equivalent. An analogous situation occurs here; expressing the natural variables of a THP in terms of those of the global Lagrangian  $\Lambda(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$ , e.g., expressing the energy  $E(\mathbf{p}_s, \mathbf{p}, \rho, \rho_s, \eta, \mathbf{x}, t)$  in terms of  $(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$  by substituting in  $E$  the functions  $\mathbf{p}_s(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$ ,  $\mathbf{p}(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$ ,  $\rho(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$ , and  $\rho_s(\mathbf{u}, \mathbf{u}_s, T, \mu, \eta, \mathbf{x}, t)$ , yields  $\Lambda$  in terms of its natural variables  $\Lambda(d\mathbf{x}/dt, d\mathbf{x}_s/dt, T(-d\eta/dt), \mu(-d\phi/dt), \eta, \mathbf{x}, t)$ . Such a Lagrangian approach leading to second-order equations will be investigated elsewhere. On the other hand, treating the natural variables and their conjugates on an equal footing, the Hamiltonian-like forms are constructed. They are analyzed below.

The following representations of  $L$  can replace it in the action functional (30’)

$$L = P(\mathbf{u}, \mathbf{u}_s, \mu, T, \nabla \mu, \nabla T, \eta, \mathbf{x}, t) - \rho_s T - \rho \mu, \quad (117a)$$

$$L = F_L(\mathbf{u}, \mathbf{u}_s, \rho, T, \nabla \rho, \nabla T, \eta, \mathbf{x}, t) - \rho_s T, \quad (117b)$$

$$L = \Gamma_L(\mathbf{u}, \mathbf{u}_s, \mu, \rho_s, \nabla \mu, \nabla \rho_s, \eta, \mathbf{x}, t) - \rho \mu. \quad (117c)$$

These lead, respectively, to the following structures of the Lagrangian  $\Lambda$ :

$$\Lambda = P(\mathbf{u}, \mathbf{u}_s, \mu, T, \nabla \mu, \nabla T, \eta, \mathbf{x}, t) - \rho_s T - \rho \mu - \rho_s \dot{\eta} - \rho \dot{\phi} - \gamma \dot{\lambda} - \gamma_s \dot{\lambda}_s, \quad (118a)$$

$$\Lambda = F_L(\mathbf{u}, \mathbf{u}_s, \rho, T, \nabla \rho, \nabla T, \eta, \mathbf{x}, t) - \rho_s T - \rho_s \dot{\eta} - \rho \dot{\phi} - \gamma \dot{\lambda} - \gamma_s \dot{\lambda}_s, \quad (118b)$$

$$\Lambda = \Gamma_L(\mathbf{u}, \mathbf{u}_s, \mu, \rho_s, \nabla \mu, \nabla \rho_s, \eta, \mathbf{x}, t) - \mu \rho - \rho_s \dot{\eta} - \rho \dot{\phi} - \gamma \dot{\lambda} - \gamma_s \dot{\lambda}_s, \quad (118c)$$



and, after using the stationarity conditions, to the general forms

$$\Lambda = P(\mathbf{u}(\nabla), \mathbf{u}_s(\nabla), \mu(-\dot{\phi}), T(-\dot{\eta}), \nabla\mu(-\dot{\phi}), \nabla T, \eta, \mathbf{x}, t) - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s, \quad (119a)$$

$$\Lambda = F_L(\mathbf{u}, \mathbf{u}_s(\nabla), \rho, T(-\dot{\eta}), \nabla\rho, \nabla T, \eta, \mathbf{x}, t) - \rho\dot{\phi} - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s, \quad (119b)$$

$$\Lambda = \Gamma_L(\mathbf{u}(\nabla), \mathbf{u}_s, \mu(-\dot{\phi}), \rho_s, \nabla\mu, \nabla\rho_s, \eta, \mathbf{x}, t) - \rho_s\dot{\eta} - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s, \quad (119c)$$

where gradient representation of definite variables has been symbolically stressed. The quantities  $P$ ,  $F_L$ , and  $\Gamma_L$  of the middle group of equations are Lagrangian-type THP's. The pressure  $P$  may be regarded as the Lagrangian of the grand potential  $\Omega$ , as it is the Legendre transform of the (extended, momenta containing) grand potential  $\Omega$  with respect to the momenta  $\mathbf{p}$  and  $\mathbf{p}_s$ . The function  $F_L$  is the free energy Lagrangian. The kinetic potential  $L$  is the Lagrangian of the energy. Here we have omitted a verification of the related Euler-Lagrange equations for THP. It is easy to show their equivalence with those obtained from the original  $L$ , but details are left to the reader. The theory does not involve difficulties provided that the required THP is given. On the other hand, great difficulties appear in carrying out the transformations when this THP has to be obtained from another one. These problems arise because the gradient representations of the momenta contain densities, which must be expressed in terms of the derivatives of the THP which is yet unknown. Close to equilibrium some approximate approach is possible [3]. However, generally it is better to work in terms of an original THP.

Here the generalization of the classical formula  $L = \mathbf{p}\cdot\mathbf{u} - E$  holds on the basis of Eq. (52), and hence

$$L = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - E(\mathbf{p}, \mathbf{p}_s, \rho, \rho_s, \nabla\rho, \nabla\rho_s, \eta, \mathbf{x}, t), \quad (120)$$

$$\Lambda = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - \rho_s\dot{\eta} - \rho\dot{\phi} - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s - E(\mathbf{p}, \mathbf{p}_s, \rho, \rho_s, \nabla\rho, \nabla\rho_s, \eta, \mathbf{x}, t). \quad (121)$$

When the first of these equations is used in the action functional (30') the field description is in terms of  $E$ , associated with  $\mathbf{p}$ ,  $\mathbf{p}_s$ ,  $T$ , and  $\mu$  in appropriate Clebsch representations, resulting, as always, from the stationarity conditions on the action  $A$ . The link with the Lagrangian description of motion is made by the equation

$$\Lambda = \mathbf{p}\cdot\dot{\mathbf{x}} + \mathbf{p}_s\cdot\dot{\mathbf{x}}_s - \rho_s\dot{\eta} - \rho\dot{\phi} - E(\mathbf{p}, \mathbf{p}_s, \rho, \rho_s, \nabla\rho, \nabla\rho_s, \eta, \mathbf{x}, \mathbf{x}_s, t), \quad (122)$$

where the velocity definitions  $\mathbf{u} = d\mathbf{x}/dt$  and  $\mathbf{u}_s = d\mathbf{x}_s/dt$  have been used to replace the momentum-multiplier term (with  $\mathbf{p}$ ,  $\mathbf{p}_s$ ,  $\lambda$ , and  $\lambda_s$ ) of Eq. (121), and all the intensities are in terms of the total time derivatives of the generalized state:  $\mathbf{x}$ ,  $\mathbf{x}_s$ ,  $\eta$ ,  $\phi$ ,  $\lambda$ , and  $\lambda_s$ . This implies a general Fermat principle for distributed systems

$$\delta\Lambda = \delta \int_{t_1}^{t_2} \{ [\mathbf{p}\cdot d\mathbf{x} + \mathbf{p}_s\cdot d\mathbf{x}_s - \rho_s d\eta - \rho d\phi - E(\mathbf{p}, \mathbf{p}_s, \rho, \rho_s, \nabla\rho, \nabla\rho_s, \eta, \mathbf{x}, \mathbf{x}_s, t) dt] dV \} = 0. \quad (123)$$

Its lumped version, obtained after integrating of the above equation with respect to the volume in a homogeneous case, is

$$\delta\Lambda = \delta \int_{t_1}^{t_2} \{ [\mathbf{P}\cdot d\mathbf{x} + \mathbf{P}_s\cdot d\mathbf{x}_s - Sd\eta - Md\phi - E(\mathbf{P}, \mathbf{P}_s, M, S, \eta, \mathbf{x}, \mathbf{x}_s, t) dt] \} = 0, \quad (124)$$

where all the extensive quantities are referred to the whole system. Since the integration volume  $V$  was completely arbitrary (not necessarily that of a system with constant mass) a generalization of this equation for the system with variable mass (e.g., chemical rocket engine) is immediate. It requires only explicit dependence of  $E$  on  $\phi$ .

Still other potentials can be considered. Since the temperature and mass density are frequently met variables, the free energy seems to be a useful THP of energy type. It appears in the following representations of  $L$  and  $\Lambda$ :

$$L = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - T\rho_s - F(\mathbf{p}, \mathbf{p}_s, \rho, T, \nabla\rho, \nabla T, \eta, \mathbf{x}, t), \quad (125)$$

$$\Lambda = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - T\rho_s - \rho_s\dot{\eta} - \rho\dot{\phi} - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s - F(\mathbf{p}, \mathbf{p}_s, \rho, T, \nabla\rho, \nabla T, \eta, \mathbf{x}, t), \quad (126)$$

where again Clebsch representations are generated from  $\Lambda$ . For example, while there is no stationarity condition for  $L$  with respect to  $\rho_s$ , the global Lagrangian  $\Lambda$  yields such a condition in the Clebsch form  $T = -d\eta/dt$ , because  $\rho_s$  appears in the constraint term of  $\Lambda$ . Indeed,  $\Lambda$ , not  $L$ , governs the process. In the free energy formalism the complexity of temperature, Eq. (37), disappears since  $T$  becomes an independent variable. Instead, the entropy density  $\rho_s = -\partial F/\partial T$  (contained in the gradient representations of the momenta) can be a very complex function. This kind of complexity appears also for the grand potential where the densities  $\rho$  and  $\rho_s$  must be presented in terms of  $-\partial\Omega/\partial T$  and  $-\partial\Omega/\partial\mu$ .

The grand potential  $\Omega$  is the Legendre transform of  $E$  with respect to  $\rho_s$  and  $\rho$ , or that of  $L$  with respect to  $\rho_s$ ,  $\rho$ ,  $\mathbf{u}_s$ , and  $\mathbf{u}$ ; hence

$$L = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - T\rho_s - \mu\rho - \Omega(\mathbf{p}, \mathbf{p}_s, \mu, T, \nabla\mu, \nabla T, \eta, \mathbf{x}, t), \quad (127)$$

$$\Lambda = \mathbf{p}\cdot\mathbf{u} + \mathbf{p}_s\cdot\mathbf{u}_s - T\rho_s - \mu\rho - \rho_s\dot{\eta} - \rho\dot{\phi} - \gamma\dot{\lambda} - \gamma_s\dot{\lambda}_s - \Omega(\mathbf{p}, \mathbf{p}_s, \mu, T, \nabla\mu, \nabla T, \eta, \mathbf{x}, t). \quad (128)$$

The formula for  $\Gamma$ , the THP involving the transformation with respect to mass density and momenta, is omitted.

**X. DYNAMICS  
THROUGH THE FUNDAMENTAL EQUATION II—  
POISSON BRACKET FORMALISM**

The energy form (66) of the action  $A$  is very useful as it constitutes the basis for the powerful Poisson bracket formalism involving  $H$  rather than  $L$  or  $\Lambda$ . Since  $H$  of Eq. (66) does not contain time derivatives of Clebsch variables, the three-dimensional integral of the total energy plays an essential role in the functional bracket formulation. Using Eqs. (67) through (71), the Euler-Lagrange equations of the functional (66) in terms of the density  $H$  can be written in the canonical form

$$\delta\rho: -\frac{\partial\phi}{\partial t} = \frac{\delta H}{\delta\rho_s} \quad [ = \mu(\rho, \rho_s, \eta, \mathbf{x}, t) + (\mathbf{u} \cdot \nabla)\phi = \mu^+ - \alpha(\mathbf{u} \cdot \nabla)\lambda ], \quad (129)$$

$$\delta\phi: -\frac{\partial\rho}{\partial t} = -\frac{\delta H}{\delta\phi} \quad ( = \nabla \cdot \rho\mathbf{u} ), \quad (130)$$

$$\delta\rho_s: -\frac{\partial\eta}{\partial t} = \frac{\delta H}{\delta\rho_s} \quad [ = T(\rho, \rho_s, \eta) + (\mathbf{u}_s \cdot \nabla)\eta = T^+ - \alpha_s(\mathbf{u}_s \cdot \nabla)\lambda_s ], \quad (131)$$

$$\delta\eta: -\frac{\partial\rho_s}{\partial t} = -\frac{\delta H}{\delta\eta} \quad ( = \nabla \cdot \rho_s\mathbf{u}_s - \Phi - \Psi ), \quad (132)$$

$$\delta\gamma: -\frac{\partial\lambda}{\partial t} = \frac{\delta H}{\delta\gamma} \quad [ = -(\mathbf{u} \cdot \nabla)\lambda ], \quad (133)$$

$$\delta\lambda: -\frac{\partial\gamma}{\partial t} = -\frac{\delta H}{\delta\lambda} \quad ( = \nabla \cdot \gamma\mathbf{u} ), \quad (134)$$

$$\delta\gamma_s: -\frac{\partial\lambda_s}{\partial t} = \frac{\delta H}{\delta\gamma_s} \quad [ = -(\mathbf{u}_s \cdot \nabla)\lambda_s ], \quad (135)$$

$$\delta\lambda_s: -\frac{\partial\gamma_s}{\partial t} = -\frac{\delta H}{\delta\lambda_s} \quad ( = \nabla \cdot \gamma_s\mathbf{u}_s ). \quad (136)$$

The expressions in square brackets and parentheses verify this Hamiltonian representation for the fluid Hamiltonian (65), or the energy  $E$ , Eqs. (54) or (55), in which the gradient representations of the velocities or momenta have been substituted. Indeed, the equations obtained are equivalent to the stationarity conditions on  $A$  obtained from the kinetic potential  $L$ , Eqs. (13), (14), (15'), (16'), and (31) through (44). Their Poissonian form is

$$\frac{\partial\phi}{\partial t} = \{ \phi, H \} = \frac{\delta H}{\delta\rho}, \quad (137)$$

$$\frac{\partial\rho}{\partial t} = \{ \rho, H \} = \frac{\delta H}{\delta\phi}, \quad (138)$$

$$\frac{\partial\eta}{\partial t} = \{ \eta, H \} = \frac{\delta H}{\delta\rho_s}, \quad (139)$$

$$\frac{\partial\rho_s}{\partial t} = \{ \rho_s, H \} = \frac{\delta H}{\delta\eta}, \quad (140)$$

$$\frac{\partial\lambda}{\partial t} = \{ \lambda, H \} = \frac{\delta H}{\delta\gamma}, \quad (141)$$

$$\frac{\partial\gamma}{\partial t} = \{ \gamma, H \} = \frac{\delta H}{\delta\lambda}, \quad (142)$$

$$\frac{\partial\lambda_s}{\partial t} = \{ \lambda_s, H \} = \frac{\delta H}{\delta\gamma_s}, \quad (143)$$

$$\frac{\partial\gamma_s}{\partial t} = \{ \gamma_s, H \} = \frac{\delta H}{\delta\lambda_s}, \quad (144)$$

for the Hamiltonian density (65). This canonical Hamiltonian system can be written in the form

$$(-\phi_{,t}, -\rho_{,t}, -\eta_{,t}, -\rho_{s,t}, -\lambda_{,t}, -\gamma_{,t}, -\lambda_{s,t}, -\gamma_{s,t})^T = \mathbf{B} \left[ \frac{\delta H}{\delta\phi}, \frac{\delta H}{\delta\rho}, \frac{\delta H}{\delta\eta}, \frac{\delta H}{\delta\rho_s}, \frac{\delta H}{\delta\lambda}, \frac{\delta H}{\delta\gamma}, \frac{\delta H}{\delta\lambda_s}, \frac{\delta H}{\delta\gamma_s} \right]^T, \quad (145)$$

where  $\mathbf{B}$  is the Hamiltonian matrix

$$\mathbf{B} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \end{pmatrix}. \quad (146)$$

Through transformations of the Hamiltonian matrix [23], the theory of Poisson brackets allows a passage from the canonical field equations used here into another equivalent set of field equations, expressed in terms of various physical variables, associated with the noncanonical Poissonian brackets. For example, one can replace the variables  $\eta$  and  $\phi$  of the above set by the momentum densities  $\mathbf{p}$  and  $\mathbf{p}_s$ , gaining information about the equations of motion, c.f. Eq. (90).

**XI. TESTING MODELS OF ENTROPY SOURCES**

One can correctly argue that those of our results which do not pertain to any particular model are more valuable than those that are based on the specific forms of the entropy generation in the Lagrangian. This is because we still know too little about dissipation and dissipative potentials. However, the generality of Eqs. (129)–(146) constitutes an excellent tool for investigating various positive expressions for entropy sources. By changing the analytical form of  $\sigma_s$  in the chosen kinetic potential  $L$ , the gradient representations of the velocities and momenta are changed and hence various Hamiltonians  $H$  and related equations of motion can be obtained. Those forms of  $\sigma_s$  which lead to the best agreement between experiments and the resulting energy and equations of motion are, heuristically, the most appropriate models of dissipation in the framework of the present theory. The aptness of the Onsager model, based as it is on the dissipation potentials, and its extensions and modifications can also be tested in this way. A tool is therefore obtained to

test models for dissipation. Such tests are planned to be presented in a future paper.

## XII. FINAL REMARKS

What has been achieved in this development?

(1) A unification of first and second law of thermodynamics in the context of the extremal behavior of action (on the example of heat transfer in fluids) where the matter and the entropy are the two basic independent entities.

(2) A mathematical method of simultaneous derivation and synthesis of conservation laws and equations of transport, within a generalized Hamilton's principle including dissipative terms and still leading to the canonical formalism (transformation theory of the Poisson brackets).

(3) Introduction of a view of heat and dissipative work as effects of the transport of the entropy in the fluid frame.

(4) A thermodynamic method unifying hydromechanics and thermodynamics within the context of the extended thermohydrodynamic potentials, obeying Legendre transformations with respect to both mechanical and thermodynamical variables.

(5) A proof that the energy  $E$  of the action approach,

while (in Onsager's scheme) numerically equal to  $E^{\text{class}}$  of statistical mechanics, is not the same function as the  $E^{\text{class}}$  that generates an irreversible motion due to presence of certain extra terms in  $E$ . These terms may vanish along the path making  $E = E^{\text{class}}$ , but since their derivatives are generally nonvanishing, certain additional terms appear in the equations of motion that preserve dissipation. Onsager's potentials are not necessarily the simplest and most effective in this theoretical scheme, and other dissipation models can be tested, for example, a model in which the generation of the entropy resembles a chemical reaction.

(6) A supposition that far from equilibrium the energy and conservation laws may have forms different from those currently accepted, with the thermal phase playing an essential role. This problem is associated with the definition of the nonequilibrium temperature. Stability properties of such new  $E$  around equilibrium should be proven, in order to make it an admissible physical candidate.

## ACKNOWLEDGMENT

The authors wish to acknowledge partial support of this work by the U.S. Department of Energy, under Contract No. DOE-FG02-86ER13488.

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