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Field thermodynamic potentials and geometric thermodynamics with heat transfer and fluid flow

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In order to treat the effects of local nonequilibrium in fluids the thermodynamic metric, previously used for measuring dissipation, is extended from a space of extensive state variables into a space of the field variables involving nonequilibrium quantities such as heat flux. The metric is investigated in the context of the field description of transport and flow phenomena off but close to equilibrium. Thermodynamic potentials and corresponding tensors are constructed on the basis of the extended Gibbs equation involving heat and macroscopic velocity terms. An extension of the theory is suggested to the problem of multicomponent heat and mass diffusion.

I. INTRODUCTION

Classical thermodynamics usually deals with changes through equilibrium states. However, the possibility of defining invariant nonequilibrium temperatures and pressures[1] opens the way for dealing consistently with *nonequilibrium* transitions, by continuing to use standard classical thermodynamic methods[2] based on Gibbs's equation, thermodynamic potentials, and variable transformations. A generalized Gibbs equation involving heat terms was obtained[1] with nonequilibrium intensive parameters invariant with respect to change of the irreversible variable; the approach was through Hamilton's principle. The many treatments using this approach previously[3-7] were restricted to fluids in equilibrium, where the problem of invariance of thermodynamic intensities out of equilibrium does not appear. The consistency of the results of a variational approach[1] with the kinetic theory and the solution of Boltzmann equation[8] supports the possibility of a purely macroscopic description of transitions through nonequilibrium states not far from Gibbs's equilibrium manifold.

In this work, we apply the extended Gibbs equation obtained in Ref. 1 to the problem of heat transfer[9] in the context of differential geometry,[10] in particular of thermodynamic length.[11,12] The concept of length in thermodynamics has proved fruitful in many investigations: the invariant formulation of the (equilibrium) fluctuation theory,[12] interactions in equilibrium,[12] and nonequilibrium fluids[9] described by either classical[2] or extended[9,13,14] thermodynamics, stability problems,[15] bounds on dissipation,[14] and stochastic interpretations.[16] Care must be used in the interpretation of thermodynamic metrics, particularly of the spaces in which they are valid and of lengths and areas connected with those metrics.[17] Nonetheless, the usefulness of the approach thus far encourages us to try to extend it, particularly to nonequilibrium systems, in view of its close connection with dissipation.

The discussion proceeds as follows. The macroscopic formalism leading to the nonequilibrium Gibbs equation[11] is recapitulated in Sec. II on the basis of Ref. 1, with emphasis on the inclusion of variables adequate for the description of the disequilibrium of interest. Some aspects of the problem of reference states for nonequilibrium systems, and thermodynamic curvature caused by heat,[9] are discussed in Sec. III. Section IV reviews the roles of classical (equilibrium) thermodynamic potentials V and discusses the so-called copotentials, the complete Legendre transformations of V for systems of given size. Fluids in motion are treated in Sec. V in the context of nonequilibrium length of thermodynamic field theory and the classical thermodynamic potentials and thermodynamic tensors are extended to include heat transfer and convection. Thermodynamic stability conditions for equilibrium in the extended state space involving flow variables are given in Sec. VI. In the conclusion, Sec. VII, we show the correspondence between the thermodynamic potentials used in equilibrium and nonequilibrium situations not far from Gibbs surface and the direct generalization of the theory to mass diffusion in multicomponent systems.

For the thermodynamics pursued here the definition of Gibbs's surface is essential, even though this is not the surface on which thermodynamic length is measured.[18,19] For the extended $n+m+1$ state space involving n classical (static) variables, m flow variables, and the energy potential E, the Gibbs surface is the n-dimensional equilibrium submanifold corresponding to the classical relation between E and the other classical variables when all the flow variables vanish. That is, the Gibbs surface is the submanifold $E(\rho,\rho_s,0,0)$ in the space of densities of matter, entropy, and momenta, and the flux variables $\mathbf{I}$ and $\mathbf{J}$ when $\mathbf{I}=\mathbf{J}=0$.

II. NONEQUILIBRIUM KINETIC POTENTIAL, THERMAL ENERGY, AND MOMENTUM

For a one-component fluid out of but not far from equilibrium, described by the specific entropy s, specific internal energy $\mathbf{e}$, and mass density ρ (or specific volume $v=\rho^{-1}$), a thermal kinetic potential exists[1] based on the velocity of the entropy diffusion $\mathbf{v}_s$ and the hydrodynamic velocity $\mathbf{u}$. When expressed in terms of the more popular variables of entropy density $\rho_s = \rho s$ and entropy flux in the fluid frame $\mathbf{j}_s$ (heat flux $\mathbf{q} = \mathbf{j}_s / T$), this velocity is $\mathbf{v}_s = \mathbf{j}_s / \rho_s = \mathbf{q}(\rho s T)^{-1}$. It appears as an extra variable in the kinetic potential density of the flowing fluid,[1]

$$L(\rho, s, \mathbf{u}, \mathbf{v}_s) = \rho \frac{\mathbf{u}^2}{2} + \rho g s^2 \frac{\mathbf{v}_s^2}{2} - \rho e(\rho, s) \; , \tag{1}$$

where the term containing g is related to heat phenomena. From (1) one can define the "differential" thermal kinetic potential referred to unit entropy of a nonequilibrium fluid as[1]

$$\begin{aligned} l_s &\equiv \left[\frac{\partial L}{\rho \partial s} \right]_s = \left[\frac{\partial L}{\rho \partial s} \right]_{\rho, \mathbf{v}_s, \mathbf{u}} \\ &= - \left[T(\rho, s) - g s \mathbf{v}_s^2 - \frac{\partial g}{\partial s} s^2 \frac{\mathbf{v}_s^2}{2} \right] \; , \end{aligned} \tag{2}$$

which is a useful quantity to extract heat phenomena from the total hydrothermodynamic behavior. Here $T(\rho, s) = T^{\text{eq}}$ is the equilibrium energy function, known from classical thermodynamics, expressed in terms of its natural variables,[2] and $g(\rho, s)$ is an "inertial coefficient" associated with the deviation of internal energy (or entropy) from local equilibrium. For a hard-sphere Boltzmann gas g is a constant equal to $2m^2/5k^2$; this expression is a consequence of the solution of Boltzmann kinetic equation.[1] For real fluids the general definition of $g(\rho, s)$, in terms of the nonequilibrium internal energy e, is the derivative $\rho^2 \partial^2 e / \partial \mathbf{j}_s^2$; some information of how to compute g in the general case is given in Ref. 1. For the purposes of this work an implicit function $\mathbf{g}(\rho, s)$ is enough. In our close-to-equilibrium theory every multiplicative coefficient of any kinetic term can be taken as function of the classical parameters only.[1] The quantity $(-l_s)$ is the coefficient linking the heat flux $\mathbf{q}$ to the entropy flux $\mathbf{j}_s$ in the expression for the total energy flux when the Lagrangian formalism[1] in the variables $\rho, \mathrm{s}, \mathbf{v}_s, \mathbf{u}$ is applied to obtain the components of the energy-momentum tensor, in particular energy flux. Thus the quantity $-l_s \equiv T(\rho, s, \mathbf{v}_s)$ has the interpretation of a nonequilibrium temperature. This quantity (as well as other thermodynamic intensities of this kind) is used in this work to construct the consistent formalism of an extended thermodynamics in which $T(\rho, \mathrm{s}, \mathbf{v}_s)$ appears as the partial derivative of the energy with respect to the entropy in the extended Gibbs formula involving fluid flow and heat phenomena.

As shown in Ref. 1 the energy function associated with the kinetic potential (1), i.e., the Legendre transform of L with respect to both velocities $\mathbf{v}_s$ and $\mathbf{u}$, is the total energy density of the flowing nonequilibrium fluid with heat

$$E = \rho \frac{\mathbf{u}^2}{2} + \rho g s^2 \frac{\mathbf{v}_s^2}{2} + \rho e(\rho, s) \tag{3}$$

and the derivative $\mathbf{I} = \partial L / \partial \mathbf{v}_s$ is the corresponding density of a generalized momentum ("thermal momentum" in Ref. 1) which exists due to heat transfer (or entropy transfer) in the fluid even if the fluid is at rest (corresponding to vanishing hydrodynamic velocity $\mathbf{u} = 0$). From Eq. (1)

$$\mathbf{I} \equiv \frac{\partial L}{\partial \mathbf{v}_s} = \rho g s^2 \mathbf{v}_s = g s \mathbf{j}_s = \rho^{-1} g \rho_s^2 \mathbf{v}_s \; . \tag{4}$$

When energy and momenta pertain to the unit mass of a continuum, the units of $e = E/\rho$ and $\mathbf{i} = \mathbf{I}/\rho$ are $(\text{m/sec})^2$ and m/sec, respectively. However, it was shown[1] that when heat phenomena are considered, expressing energy, thermal momentum, and other quantities per unit of entropy is both natural and suitable; i.e., the quantities $e_s \equiv E/\rho_s$ and $\mathbf{i}_s \equiv \mathbf{I}/\rho_s$ are particularly natural. They have dimensions of temperature K and K sec/m, respectively. They may be used in turn with specific quantities or volumetric quantities when the Gibbs equation is established; the volumetric quantities have been the most popular in thermodynamic descriptions. The special role of the entropy basis in the description of heat phenomena results from its role in Hamilton's principle[1,3-7] where entropy and mass are the two basic entities of the hydrothermodynamic behavior of a continuum and the heat can be viewed as the transport of entropy in the frame of the moving fluid.[1]

The energy density E, Eq. (3), expressed as a function of its natural variables of momentum densities $\mathbf{I}$ and $\mathbf{J} \equiv \rho \mathbf{u}$, is

$$E(\rho, \rho_s, \mathbf{I}, \mathbf{J}) = \rho e(\rho_s, \rho) + \rho g^{-1} \rho_s^{-2} \mathbf{I}^2 / 2 + \rho^{-1} \frac{\mathbf{J}^2}{2} \; . \tag{5}$$

This is a Hamiltonian type of function. The velocity of the entropy diffusion $\mathbf{v}_s$ is obtained from (5) by differentiating E with respect to $\mathbf{I}$, which conforms to the general formula $\mathbf{v} = \partial H / \partial \mathbf{p}$ for a Hamiltonian $\mathbf{H}$. One obtains $\mathbf{v}_s \equiv \rho g^{-1} \rho_s^{-2} \mathbf{I}$ in agreement with Eq. (4). The heat flux density $\mathbf{q}$ can be then computed as

$$\mathbf{q} = T \mathbf{j}_s = T \rho s \mathbf{v}_s = T \rho (g s)^{-1} \mathbf{i} = T (g s)^{-1} \mathbf{I} \; . \tag{6}$$

At equilibrium $\mathbf{I}$, $\mathbf{j}_s$, and $\mathbf{q}$ vanish; hence the thermal momentum appears only for nonequilibrium fluids. It can be associated with the Cattaneo form of the equation of heat conduction,[1,13] which replaces the (less exact) Fourier equation $\mathbf{q} = -\lambda \nabla T$. From Eqs. (5) and (6) the nonequilibrium part of the specific internal energy is

$$\Delta e = (g s^2)^{-1} \mathbf{i}^2 / 2 = \tfrac{1}{2} g \mathbf{q}^2 / \rho^2 T^2 \; , \tag{7}$$

which corresponds to the nonequilibrium decrease of the specific entropy

$$\Delta s = -\Delta e / T = -\tfrac{1}{2} (g \mathbf{q}^2 / \rho^2 T^3) \; . \tag{8}$$

For an ideal gas for which $g = 2m^2/5k^2$ and $P = \rho k T / m$,

$$\Delta s = -(m / 5 \rho P k T^2) \mathbf{q}^2 \tag{8a}$$

in accordance with the well-known results of the kinetic theory[8] and extended irreversible thermodynamics (EIT).[13] In fact, the origin of the kinetic potential Eq. (1) is in kinetic theory.[1] Once it is formulated, however, it is a very suitable starting point for description of heat transfer away from local equilibrium when a phenomenological description is pursued, even for dense gases and polyatomic fluids.

From the invariance of nonequilibrium temperatures and pressures with respect to transformations of the nonequilibrium variables in the energy-momentum tensor of the fluid, e.g., $\mathbf{j}_s \rightarrow \mathbf{I}$, it was shown[1] that the thermal momentum $\partial L/\partial \mathbf{v}_s$ is the appropriate nonequilibrium variable to be kept constant when differentiating nonequilibrium energy with respect to the entropy and volume. Only when thermal momentum $\mathbf{I}$ is used do the two definitions of nonequilibrium temperature, the thermodynamic $(\partial E/\partial \rho_s)_{\rho,\mathbf{I},\mathbf{J}}$ and the dynamic $\mathbf{q}/\mathbf{j}_s$ coincide. Other nonequilibrium variables such as $\mathbf{q}$ and $\mathbf{j}_s$ do not have this property:[1] they lead to different values of T and P which depend on what is kept constant in the energy formulas. The unique role of the thermal momentum results from the fact that the momenta are the natural variables of energy.[1] Consequently, in this work we use the nonequilibrium temperature defined as

$$
\begin{aligned}
T(\rho,\rho_s,\mathbf{I}) &= \left[\frac{\partial E}{\partial \rho_s}\right]_{\rho,\mathbf{I},\mathbf{J}} = -\left[\frac{\partial L}{\partial \rho_s}\right]_{\rho,\mathbf{v}_s,\mathbf{u}} \\
&= T(\rho,\rho_s) - gs\mathbf{v}_s^2 - \left[\frac{\partial g}{\partial s}\right]_{\rho} s^2 \frac{\mathbf{v}_s^2}{2} \\
&= T(\rho,\rho_s) - \rho(g\rho_s^3)^{-1}\mathbf{I}^2 \\
&\quad - \left[\frac{\partial g}{\partial s}\right]_{\rho} (g^2\rho_s^2)^{-1}\frac{\mathbf{I}^2}{2} \ . \qquad (9)
\end{aligned}
$$

With the signs as shown, this coincides with the differential kinetic potential (2). The equality of the appropriate derivatives of energy E and (negative) kinetic potential L in Eq. (9) is not accidental; it is the result of Lagrangian formalism where $(\partial E/\partial \zeta)_p = -(\partial L/\partial \zeta)_v$ for any arbitrary parameter ζ contained in E and L. This is because the Legendre transformation from L to E involves only $\mathbf{p}$ and $\mathbf{v}$, but not ζ. In mechanics the time t is used commonly for ζ, but ζ may be any variable in E or L which is neither velocity nor momentum. In our case, ζ is ρ_s.

An analogous definition holds for the nonequilibrium chemical potential μ. Now $\zeta = \rho$. For our L and E, Eqs. (1) and (3), the nonequilibrium chemical potential of a moving fluid (in Eulerian or field representation) is

$$
\begin{aligned}
\mu(\rho,\rho_s,\mathbf{I},\mathbf{J}) &= \left[\frac{\partial E}{\partial \rho}\right]_{\rho_s,\mathbf{I},\mathbf{J}} = -\left[\frac{\partial L}{\partial \rho}\right]_{\rho_s,\mathbf{v}_s,\mathbf{u}} \\
&= \mu(\rho,\rho_s) - \frac{\mathbf{u}^2}{2} + \tfrac{1}{2} g s^2 \mathbf{v}_s^2 \left[1 - \left[\frac{\partial \ln g}{\partial \ln \rho}\right]_s + \left[\frac{\partial \ln g}{\partial \ln s}\right]_{\rho}\right] \\
&= \mu(\rho,\rho_s) - \rho^{-2}\frac{\mathbf{J}^2}{2} + \tfrac{1}{2}(g\rho_s^2)^{-1}\mathbf{I}^2 \left[1 - \left[\frac{\partial \ln g}{\partial \ln \rho}\right]_s + \left[\frac{\partial \ln g}{\partial \ln s}\right]_{\rho}\right] \ . \qquad (10)
\end{aligned}
$$

The role of convection velocity is as essential for this function as for the total energy. The sign of $\mathbf{u}^2/2$ is, however, reversed; this is associated with the concavity of μ around equilibrium in its natural frame, as we shall see in Eq. (40).

The nonequilibrium temperatures and chemical potentials used here differ from corresponding quantities introduced in Ref. 1 for the fluid at rest; some remarks concerning this matter are in order. All quantities in question are invariant with respect to the transformations of the nonequilibrium variables, $\mathbf{I} \rightarrow \mathbf{j}_s$, as they should be. However, the present formalism uses exclusively densities of all possible extensities in the formula for energy density whereas the previous formalism[1] used the thermal momenta referred to the unit of entropy. That formalism had some advantage in that $\mathbf{i}_s$, an intensive quantity, rather than $\mathbf{I}$, appears in the expressions for the entropy production of σ_s and the related equation of heat conduction, the expression $\sigma_s = -T^{-1}\mathbf{j}_s \cdot (\nabla T + \partial \mathbf{i}_s/\partial t)$. However, the present formalism consistently uses energy as a function of the extensities only in accord with the standard thermodynamic formalism based on the fundamental equation and thermodynamic transformations.[2] The differences between the two temperatures, of Ref. 1 and of this work, can be linked with the slightly different ways of splitting the energy flux between the heat flux $\mathbf{q}$ and the work of stresses resulting from the transfer of the entropy or heat,[8] $\mathbf{\Pi}_s$. For the temperatures $\tilde{T}$ of Ref. 1 the heat flux is defined as $\tilde{T}\mathbf{j}_s$ and the work of the stresses $\mathbf{\Pi}_s$ is defined as $\mathbf{\Pi}_s \cdot \mathbf{u}$ where $\mathbf{u}$ is the hydrodynamic velocity, whereas in the present work the heat flux is defined as $T\mathbf{j}_s = (\tilde{T} - \mathbf{i}_s \cdot \mathbf{v}_s)\mathbf{j}_s$, where T obeys Eq. (9), and the work of the stresses is $\mathbf{\Pi}_s \cdot (\mathbf{u} + \mathbf{v}_s) = \mathbf{\Pi}_s \cdot \mathbf{u}_s$, where $\mathbf{u}_s$ is the absolute "entropy velocity" associated with the entropy transfer or the ratio of the total entropy flux $\mathbf{J}_s$ to the entropy density ρ_s. While defining the entropy stress work as $\mathbf{\Pi}_s \cdot \mathbf{u}_s$ seems to be more appropriate in the present context than as $\mathbf{\Pi}_s \cdot \mathbf{u}$, the sum of the heat and work terms in question remains identical for the two cases.

III. NONEQUILIBRIUM EFFECTS AND THERMODYNAMIC CURVATURE

A. Nonequilibrium and reference states

For the fluid at rest, i.e., for hydrodynamic velocity $\mathbf{u} = 0$, the specific energy counterpart of Eq. (5) is

$$e(s,v,\mathbf{i})=e^{\mathrm{eq}}(s,v)+\eta(s,v)\mathbf{i}^2/2 , \qquad (5')$$

where $\eta(s,v)=[g(s,v)s^2]^{-1}$. It is associated with the Gibbs equation

$$de=Tds-pdv+\mathbf{v}_s\cdot d\mathbf{i} , \qquad (11)$$

where the velocity of entropy diffusion results from Eq. (4) and definition of η. The nonequilibrium temperature T and pressure P deviate from their corresponding (isentropic, isochoric) equilibrium values according to formulas (with $g_s=\partial g/\partial s$, $g_v=\partial_g/\partial_v, \ldots$, $\eta_s\equiv\partial\eta/\partial s$, $\eta_v\equiv\eta/\partial v$, etc.):

$$\begin{aligned}T(s,v,\mathbf{i})&=T(s,v)+\eta_s\mathbf{i}^2/2\\&=T(s,v)-(g_s/2+g/s)(\mathbf{q}/\rho T)^2 , \qquad (9')\end{aligned}$$

equivalent to Eq. (9), and

$$P(s,v,\mathbf{i})=P(s,v)-\eta_v\mathbf{i}^2/2=P(s,v)+g_v(\mathbf{q}/\rho T)^2/2 , \quad (12)$$

resulting from (5′) and (6). [See Fig. 1 where $e(s,v,\mathbf{i}_s)\equiv\tilde{e}$, at point A and $e(s,v)\equiv e$, at point B, etc; the tildes designate disequilibrium according to the convention used in Ref. 1. In this text, where the complete set of variables for thermodynamic functions is specified, it is not necessary to use tildes. Also, we use abbreviated notation, $T(s,v)$ or T^{eq} instead of $T(s,v,0)$, etc.] When expressed in terms of the specific thermal momentum $\mathbf{i}$ the specific nonequilibrium entropy $s(e,v,\mathbf{i})$ is

$$\begin{aligned}s(e,v,\mathbf{i})&=s(e,v)-[g(e,v)Ts^2(e,v)]^{-1}\mathbf{i}^2/2\\&=s(e,v)-\beta(e,v)\mathbf{i}^2/2 , \qquad (13)\end{aligned}$$

where $\beta(e,v)\equiv[g(e,v)Ts^2]^{-1}$. The generalized Gibbs equation describing this entropy is

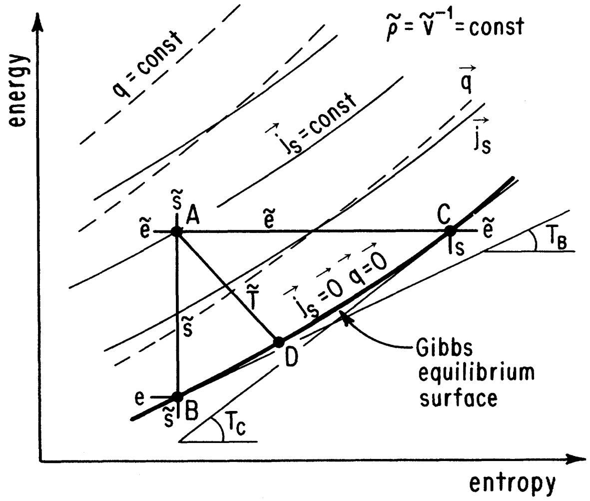

FIG. 1. Arbitrariness of the equilibrium reference states attained from given nonequilibrium state, point A. If, for example, entropy is held constant in the relaxation process or in defining the reference equilibrium, then point B is the equilibrium, but if energy is constrained to be constant, then point C is the appropriate equilibrium.

$$ds=T^{-1}de+PT^{-1}dv-T^{-1}\mathbf{v}_s\cdot d\mathbf{i} . \qquad (14)$$

Here, on the basis of (13) and (6),

$$\begin{aligned}T^{-1}(e,v,\mathbf{i})&=T^{-1}(e,v)-\left[\frac{\partial(Ts^2g)^{-1}}{\partial e}\right]\frac{\mathbf{i}^2}{2}\\&=T^{-1}(e,v)-g^2\left[\frac{\partial(Ts^2g)^{-1}}{\partial e}\right]\frac{(s\mathbf{q}/\rho T)^2}{2}\\&=T_{\mathrm{eq}}^{-1}-\beta_e\mathbf{i}^2/2 , \qquad (15)\end{aligned}$$

$$\begin{aligned}(PT^{-1})(e,v,\mathbf{i})&=(PT^{-1})(e,v)-\left[\frac{\partial(Ts^2g)^{-1}}{\partial v}\right]\frac{\mathbf{i}^2}{2}\\&=(PT^{-1})(e,v)\\&\quad-g^2\left[\frac{\partial(Ts^2g)^{-1}}{\partial v}\right]\frac{(s\mathbf{q}/\rho T)^2}{2}\\&=(PT^{-1})_{\mathrm{eq}}-\beta_v\mathbf{i}^2/2 . \qquad (16)\end{aligned}$$

One can represent differences of (15) and (16) in terms of ΔT and ΔP rather than ΔT^{-1} and $\Delta(\rho T^{-1})$ to show explicitly that they differ from those given by Eqs. (11) and (12). For the ideal hard-sphere gas (g = const) one finds,[1] for instance,

$$T(s,v,\mathbf{i})=T(s,v)-(gs)^{-1}(\mathbf{i}/s)^2 \qquad (17)$$

and

$$P(s,v,\mathbf{i})=P(s,v) \quad (\eta_v{}^{\mathrm{id\,gas}}\equiv 0) \qquad (18)$$

but, at the same time

$$T(e,v,\mathbf{i})=T(e,v)+T^2(e,v)\beta_e\mathbf{i}^2 \quad (\mathbf{u}\equiv\mathbf{0}) \qquad (19)$$

and

$$P(e,v,\mathbf{i})=P(e,v)+[\beta_e PT(e,v)-\beta_v]\mathbf{i}^2 . \qquad (20)$$

Apparently Eqs. (17) and (19) and also Eqs. (18) and (20) are in contradiction. However, there is no error in formulas (17)–(20). As it was comprehensively explained in Ref. 1, the difference pertains not to the nonequilibrium parameters but to the equilibrium (reference) parameters because *the equilibria attained from the same nonequilibrium state along isentropic and isoenergetic lines differ*, as shown in Fig. 1. This fact causes different "nonequilibrium corrections" in the two cases. In other words, the splitting of any nonequilibrium quantity (T, P, e, etc., derived for point A, Fig. 1) into an equilibrium quantity (derived for points B, C, D, etc.) and a kinetic correction ($\mathbf{q}^2$ term), which depends on the representation used for the thermodynamics. The nonequilibrium quantities (T, P, etc.) at point A, Fig. 1, only have an unambiguous, physical meaning when there is heat in the system (due to the heat flow, point A never lies on the equilibrium line BCD).

B. Thermodynamic curvature

Let us consider now the effect of heat on thermodynamic curvature.[3] Again we designate $(gTs^2)^{-1}$, Eq. (13), as β, and its derivatives with subscripts. The second differential of the specific entropy (13), in the presence of a heat flux in the system, is

$$d^2s=\left[\frac{\partial T^{-1}}{\partial e}\right](\delta e)^2+\left[\frac{\partial T^{-1}P}{\partial v}\right](\delta v)^2 +2\left[\frac{\partial T^{-1}}{\partial v}\right]\delta e\,\delta v -\beta\delta\mathbf{i}\cdot\delta\mathbf{i}-2\mathbf{i}\cdot\beta_e\delta e\,\delta\mathbf{i}-2\mathbf{i}\beta_v\delta v\cdot\delta\mathbf{i}\ . \tag{21}$$

(Maxwell relations were used to obtain this formula.) A comparison with the classical results without heat can be made if one restricts the calculation to the subspace of the variables e and v. For an ideal gas Eq. (2) yields

$$d^2s_{(\mathbf{I}=\mathrm{const})}=-\begin{bmatrix}\delta e\\ \delta v\end{bmatrix}^{\dagger}\begin{bmatrix}1/c_vT^2+\beta_{ee}\mathbf{i}^2/2 & \beta_{ev}\mathbf{i}^2/2\\ \beta_{ev}\mathbf{i}^2/2 & P/Tv+\beta_{vv}\mathbf{i}^2/2\end{bmatrix}\begin{bmatrix}\delta e\\ \delta v\end{bmatrix}\ . \tag{22}$$

For $\mathbf{i}=0$ or $\mathbf{q}=0$ the matrix of $d^2s_{(i=\mathrm{const})}$, Eq. (22), simplifies to the well-known local equilibrium expression.[10] Equation (22) has a structure identical to that of Eq. (7) obtained by Casas-Vazquez and Jou[9] with the thermal momentum $\mathbf{i}$ replacing the heat flux $\mathbf{q}$ and the coefficient $\beta=(gTs^2)^{-1}$ replacing their coefficient $\alpha=\tau v/\lambda T^2$. For the ideal gas $\alpha=\frac{27}{20}(k/m)v^2e^{-3}$. Therefore, by using Ref. 9, we immediately obtain an approximate expression for the Gaussian curvature K, associated[12] with the metric defined by $-(M/k)d^2s$:

$$K=\tfrac{1}{2}(e^2v^2/Nc_v)\mathbf{i}^2[\beta_{ev}/ev+\tfrac{1}{2}(\beta_{evv}/e+\beta_{eev}/v)]\ , \tag{23}$$

where M is the total mass of the system $M=Nm$ and N is the total number of particles. The expression $L^2=-(M/k)d^2s$ is applicable only to quasihomogeneous systems. For large heat fluxes an integration procedure for the function $-\int\int\int(\rho/k)d^2s\,dV$ is necessary.[15] For the ideal or hard-sphere gas,

$$\mathbf{i}=\tfrac{2}{5}(m^2/k^2)(s\mathbf{q}/\rho T) \tag{24}$$

and

$$\beta=(gTs^2)^{-1}=5k^2/(2m^2Ts^2)=\tfrac{15}{4}(k^3/s^2m^3e)\ , \tag{25}$$

Since β contains $s(e,v)$ it depends on both the energy and volume, and it is not at once obvious that for the ideal gas is

$$K=0\ . \tag{26}$$

For nonideal fluids, for which both g and β depend on v as well as on e, one arrives at the result of Casas-Vazquez and Jou[9] linking K and the square of the heat flux $\mathbf{q}^2$, however with a different coefficient γ instead of $\frac{3}{2}$:

$$K=(\gamma\alpha/Nc_v)\mathbf{q}^2\ . \tag{27}$$

Here γ depends on the form of the function $g(e,v)$ and vanishes for the ideal gas. The equilibrium curvature always vanishes ($\mathbf{q}\equiv 0$ at equilibrium), whereas in nonequilibrium situations the irreversible flux makes the metric curvilinear except for the ideal gas. In a sense the effect of heat flux in a nonideal gas is similar to that caused by an interaction between molecules.[9] This conclusion is confirmed by considering the energy representation metrics based on the derivatives $\partial T/\partial s$, $\partial T/\partial v$, and $\partial P/\partial v$ obtained from Eqs. (17) and (18). For the ideal gas $g_s=g_v=0$, $T=T_{\mathrm{eq}}-(gs^3)^{-1}\mathbf{i}^2$, and $P=P_{\mathrm{eq}}$ at the same s and v, and the coefficient η of $\mathbf{i}^2$ in the energy formula (5') depends on entropy only. Hence in the equation of the type of Eq. (23) all mixed derivatives vanish and the classical result for $E=0$ must hold[12] despite any heat flow. Thus the energy representation confirms that $K=0$ for an ideal gas close to but not in equilibrium. However, K need not be zero for a nonideal gas because g_s and g_v do not vanish.

One may also consider an open system of fixed volume involving $d^2\rho_s$ (variables E, ρ, and $\mathbf{I}$) as an alternative to the closed system involving d^2s (variables e,v, and $\mathbf{i}$) just analyzed. However, the Gibbs-Duhem equation implies a conformal relation $d^2\rho_s=\rho d^2S$ between these differentials,[15] so the physical results obtained above remain valid for the open system.

IV. FIELD VARIABLES AND THERMODYNAMIC METRIC FROM A POTENTIAL

Assume that we consider a thermohydrodynamic field (a fluid with variable thermal and hydrodynamic parameters in the Eulerian representation) described by field functions $a^i(\mathbf{x},t)$, $i=1,\ldots,n$, where $a^i(\mathbf{x},t)$ are physical quantities distributed in some region Γ of the physical space-time $(\mathbf{x},t)$. Consider any twice differentiable state function of the variables $a^i=a^i(\mathbf{x},t)$, say $V(a^1,\ldots,a^n)$ and its complete negative thermodynamic Legendre transformation $V^T(a_1,\ldots,a_n)$ where a^i and a_i are linked by $a_i=\partial V/\partial a^i$. In classical thermodynamics the space $\mathbf{a}^i$ is spanned by the conventional coordinates such as energy, volume, and concentrations. The Legendre transformations used in mechanics and thermodynamics differ by sign; the transformation (28) corresponds with that used in mechanics. This is to preserve the same definition when the fluid motion (described in mechanical terms[4,5]) is considered. In the so-called extended thermodynamics,[1,9,13,14] the dimensionality of the state-space a^i is enlarged by including among the state variables such quantities as fluxes[9,13] or velocities;[14] however, the problem of metric can be stated formally in the same manner as in the classical equilibrium case. The two functions $V(a^i,\ldots,a^n)$ and $V^T(a_i,\ldots,a_n)$ in the two adjoint frames $\mathbf{a}^i$ and $\mathbf{a}_i$ obey the relations

$$V^T(a_i,\ldots,a_n)\equiv\sum_i a_i a^i - V(a^i,\ldots,a^n)\;, \tag{28}$$

$$\left[\frac{\partial^2 V}{\partial a^i \partial a^k}\right]\left[\frac{\partial^2 V^T}{\partial a_j \partial a_k}\right]=\delta^i_j\;, \tag{29}$$

$$a_i=\frac{\partial V}{\partial a^i}\;, \tag{30a}$$

$$a^i=\frac{\partial V^T}{\partial a_i}\;, \tag{30b}$$

$$da_i=\left[\frac{\partial^2 V}{\partial a^i \partial a^k}\right]da^k\;, \tag{31a}$$

$$da^i=\left[\frac{\partial^2 V^T}{\partial a_i \partial a_l}\right]da_l \tag{31b}$$

so that

$$dl^2=da^i da_i=\delta^l_k da^k da_l=da^l da_l \tag{32}$$

is the element of the square of Riemannian length. Since $a^i=a^i(\mathbf{x},t)$, the thermodynamic length along given path $\mathbf{x}(t)$ linking two given points $A(\mathbf{x},t)$ and $B(\mathbf{x},t)$ in the physical space-time can be computed in terms of $\mathbf{a}^i(A)$ and $\mathbf{a}^i(B)$. Also, distances between A and B can be found by minimization of l with respect to path. Thus the concept of thermodynamic length can be incorporated naturally into the formalism of field theory by using the functions $a^i(\mathbf{x},t)$ known from solving the hydrodynamic equations of change.[15] It is important to note that the local states of the system at A and B can be out of equilibrium if nonvanishing diffusive fluxes exist along any part of the $\mathbf{x}(t)$ path. In this way, we then have achieved a construction of nonequilibrium thermodynamic length in the Eulerian (field) representation of the fluid motion.

The two frames a^i and a_i are adjoint at each point $(\mathbf{x},t)\in\Gamma$; if the Hessian matrix of V is accepted as the matrix of the covariant tensor, then the Hessian matrix of V^T (describing the coframe) is automatically the matrix of the contravariant metric tensor. Since for given frame a^i and given nonlinear function $V(a^i,\ldots,a^n)$ the coframe can always be defined in the region of the nonsingular Hessian of V, one can always define the metric tensor with covariant coordinates $g_{ik}=\partial^2 V/\partial a^i \partial a^k$ or with contravariant coordinates $g^{ik}=\partial^2 V^T/\partial a_i \partial a_k$. In principle any arbitrary scalar function V can be used. When describing thermodynamic equilibria, however, the convex (concave) functions such as energy (entropy) and their quadratic approximations are especially suitable as they are associated with the stable macroscopic equilibria, exhibiting definite signs of the components g^{ik} in either classical or extended thermodynamic state space (Sec. VI). Furthermore, they provide the simple interpretation of the stability conditions serving as Liapunov functions.[15] (However, stability criteria can also be expressed in terms of arbitrary thermodynamic potentials.[2])

For quadratic homogeneous functions $V=\mathbf{a}^\dagger\cdot\mathbf{A}\cdot\mathbf{a}$, the equality $V=V^T$ holds, and the components of the metric tensor g_{ij} are the elements of matrix $\mathbf{A}$ and those of g^{ij} the elements of $\mathbf{A}^{-1}$. For nonlinear and nonquadratic V the transformation of variables $a^i \rightarrow a^{i'}\equiv a_i$, Eqs. (31a) and (31b), is nonlinear and this is why the cofunction V^T, Eq. (31b), does not coincide with V, Eq. (31a). In the special case of a nonhomogeneous quadratic V, transformations (31a) and (31b) are necessarily linear and V^T differs from V only by a certain linear function of state a^i, and $\mathsf{g}_{ij}=\mathbf{A}$ as well as $\mathsf{g}^{ij}=\mathbf{A}^{-1}$, as in the homogeneous quadratic case. The elementary differential formula describing the transformation of the Hessian of V from the frame a^i to the coframe $(a^{i'})\equiv a_i$

$$\frac{\partial^2 V}{\partial(a^{i'})\partial(a^{k'})}=\left[\frac{\partial a^i}{\partial(a^{i'})}\right]\left[\frac{\partial a^k}{\partial(a^{k'})}\right]\left[\frac{\partial^2 V}{\partial a^i \partial a^k}\right] + \left[\frac{\partial V}{\partial a^k}\right]\left[\frac{\partial^2 a^k}{\partial(a^{i'})\partial(a^{k'})}\right] \tag{33}$$

proves that except for the case of a homogeneous quadratic V [constant Hessians in (31) and (32)], the Hessian matrix does not transform like a tensor so that a distinction between V and V^T is generally essential. This distinction is frequently overlooked in classical thermodynamics in which, with conventional state variables, the various quadratic forms applied to investigation of stability are expressed in terms of the Hessians of the entropy or the energy. These forms are commonly called "second differentials of entropy."[2,15,20] When the coordinates are the specific energy e and volume v [consider Eq. (31) for $V=s$ and $a^i=(e,v)$], in the coordinates $a_i=(\partial s/\partial e=T^{-1},\ \partial s/\partial v=PT^{-1})$, the corresponding classical copotential is, according to Eq. (28), $V^T=[(e+Pv-Ts)/T]=\mu/T$, the Planck potential. Both V and V^T are concave in their natural variables, corresponding to equilibrium.

Schlögl was able to show some virtues of the metric defined in the space of intensities[16] not pointing out, however, that it is just the corepresentation of Ruppeiner's[12] entropy metric when the mass of the system is constant. It was, however, recognized[17] that at least one of extensive variables should be fixed to determine system size. For instance, Eq. (28) indicates that the copotential of $S(E,V,M)$ degenerates to zero when the mass of the system is not fixed, making the Hessian of copotential singular, so the metric cannot be constructed. This is because the intensities are connected by the Gibbs-Duhem equation, so they cannot all be assumed independent. However, if one constrains the problem to a system of constant mass or constant volume, the metric becomes constructible. Entropy per unit volume ρ_s of a classical system is a function of energy and mass densities $\rho_s(E,\rho)$ so that the coordinates of the coframe are T^{-1} and $-\mu T^{-1}$, and the copotential V^T is $ET^{-1}-\rho\mu T^{-1}-\rho_s=-P/T$; the role of the pressure is also particularly important in the coenergy representation, as discussed below.

Similar remarks hold for the classical metrics based on energy. The specific energy e is, in the classical case, a function of the specific entropy s and volume v; hence the coordinates are T and $-P$. When the system has only two classical degrees of freedom, the coenergy (28) is then $Ts-Pv-e=-G$, the negative of the specific Gibbs free energy $G(T,-P)$. On the other hand, if one uses volumetric energy E as a function of entropy density and mass density (mass densities in multicomponent systems), i.e., the potential $E(\rho_s,\rho)$ is taken as V, as in Eq. (28), then the copotential is $T\rho_s+\mu\rho-E=P$, the pressure in the system expressed in terms of T and μ as the covariables of ρ_s and ρ.

The role of the second differentials of the pressure in the fluid stability problems was explained well only recently by Schmid,[21] who pointed out the duality of E and P as well as the role of convexity of $P(T,\mu)$; a sample of fluid in a stable, fluctuating condition is characterized by an average pressure greater than the pressure of a quiescent sample at equilibrium. Thus fluctuations in a stable fluid have the effect of "stiffening" the fluid. The essential difference between E and P is that while E is related to the intrinsic energy, P reflects the interaction energy that the sample of fluid possesses due to its interaction with the rest of the fluid.[21]

The second differentials of equilibrium volumetric quantities have turned out to be suitable Liapunov functions for stability problems of both thermodynamics and, with some extensions, see Eq. (51), hydrodynamic problems of stability.[15,20] However, their unfortunate identification with the second differential of entropy in arbitrary frames persists in the literature. It was the purpose of the above examples to show that the Hessians of various thermodynamic potentials can constitute the same thermodynamic metric g^{ij}. More information about the transformations that can generate g^{ij} can be found in Ref. 22.

V. THE METRIC FOR NONEQUILIBRIUM FLUIDS IN MOTION

Now we can pass to more difficult examples involving moving, nonequilibrium fluids which can conduct heat. The variety of equilibrium functions V that can be used to define the classical g^{ij} leads us to seek the analogous, extended functions V for moving fluids out of but close to equilibrium, in which various diffusion phenomena can occur. Since this is precisely the problem of nonequilibrium thermodynamic potentials, in extended thermodynamics (EIT) this extension is both difficult and essential due to different roles of "kinetic" terms in different frames.[1] Let us outline the problems which appear in EIT.

First, the theory of nonequilibrium thermodynamic potentials[23] is not well developed for processes requiring the inclusion of both diffusion and viscous terms. Second, no interpretation of cofunctions V^T has been given so far when the new (flow) degrees of freedom are added to the primary V. Third, the role of kinetic terms is different in various representations (various frames) and it is not always easy to transform results from one frame to another. Finally, it is an open question whether any external fields should be included in V and treated in the same manner as other terms, or should be excluded from the metric. Concerning external fields we assume the latter alternative. In view of the limitations of general forms of nonequilibrium thermodynamic potentials, and with the Gibbs equation in particular, we restrict our treatment to flowing one-component fluids whose convection velocity is $\mathbf{u}$, with heat for which the total specific energy is given by Ref. 1,

$$\begin{aligned} e(s,v,\mathbf{u},\mathbf{i}) &= e(s,v)+\mathbf{u}^2/2+\mathbf{i}^2/2s^2g(s,v) \\ &= e(s,v)+\mathbf{u}^2/2+\tfrac{1}{2}gs^2\mathbf{v}_s^2 , \end{aligned} \tag{34}$$

which is an immediate generalization of Eq. (5′). The differential Gibbs equation associated with (34) is

$$de=Tds-Pdv+\mathbf{v}_s\cdot d\mathbf{i} , \tag{35}$$

where nonequilibrium T and p obey Eqs. (11) and (12). In order to avoid expanding into a matrix representation, in equations such as (36), submatrix notation for Cartesian vectors $\mathbf{i}_s$ and $\mathbf{u}$ and their derivatives have been used. We use bare symbols for column submatrices and symbols with the superscript dagger for row submatrices. The underlined, bracketed 1's and 0's are unit and zero submatrices, respectively. The convexity of (34) at equilibrium ($V_s=u=0$) is obvious. Recall that the coefficient $\eta\equiv(gs^2)^{-1}$. Therefore the covariant tensor

$$g_{ij}=\begin{bmatrix} \dfrac{\partial T}{\partial s} & \dfrac{\partial T}{\partial v} & \dfrac{\partial T}{\partial \mathbf{i}^\dagger} & \dfrac{\partial T}{\partial \mathbf{u}^\dagger} \\ \dfrac{-\partial P}{\partial s} & \dfrac{-\partial P}{\partial v} & \dfrac{-\partial P}{\partial \mathbf{i}^\dagger} & \dfrac{-\partial P}{\partial \mathbf{u}^\dagger} \\ \dfrac{\partial \mathbf{v}_s}{\partial s} & \dfrac{\partial \mathbf{v}_s}{\partial v} & \dfrac{\partial \mathbf{v}_s}{\partial \mathbf{i}} & \dfrac{\partial \mathbf{v}_s}{\partial \mathbf{u}} \\ \dfrac{\partial \mathbf{u}}{\partial s} & \dfrac{\partial \mathbf{u}}{\partial v} & \dfrac{\partial \mathbf{u}}{\partial \mathbf{i}} & \dfrac{\partial \mathbf{u}}{\partial \mathbf{u}} \end{bmatrix} = \begin{bmatrix} \dfrac{\partial T^{\mathrm{eq}}}{\partial s}+\dfrac{\eta_{ss}i^2}{2} & \dfrac{\partial T^{\mathrm{eq}}}{\partial V}+\dfrac{\eta_{sv}\mathbf{i}^2}{2} & \eta_s\mathbf{i}^\dagger & \mathbf{0}^\dagger \\ \dfrac{-\partial p^{\mathrm{eq}}}{\partial s}+\dfrac{\eta_{vs}i^2}{2} & \dfrac{-\partial P^{\mathrm{eq}}}{\partial v}+\dfrac{\eta_{vv}\mathbf{i}^2}{2} & \eta_v\mathbf{i}^\dagger & \mathbf{0}^\dagger \\ \eta_s\mathbf{i} & \eta_v\mathbf{i} & \eta[\underline{\mathbf{1}}] & [\underline{\mathbf{0}}] \\ \mathbf{0} & \mathbf{0} & [\underline{\mathbf{0}}] & [\underline{\mathbf{1}}] \end{bmatrix} ; \tag{36}$$

furthermore, for equilibrium the metric is always positive. Using Eq. (6) one can express $\mathbf{i}_s$ corrections in terms of heat flux, a measurable quantity. For the ideal gas, the tensor is

$$\mathsf{g}_{ik}=\begin{bmatrix} \frac{2mT}{3k}+3g^{-1}s^{-4}\mathbf{i}^2 & \frac{-2T}{V} & -2g^{-1}s^{-3}\mathbf{i}^{\dagger} & \mathbf{0}^{\dagger} \\ \frac{-2T}{3v} & \frac{5kT}{3mv^2} & 0^{\dagger} & \mathbf{0}^{\dagger} \\ -2g^{-1}s^{-3}\mathbf{i} & \mathbf{0} & \frac{5k^2s^2[\underline{1}]}{2m} & [\underline{0}] \\ \mathbf{0} & \mathbf{0} & [\underline{0}] & [\underline{1}] \end{bmatrix} . \tag{37}$$

The positive sign of $g^{-1}=5k^2/2m^2$ in Eq. (37) is a consequence of the stability of heat fluctuations in the ideal gas. On the other hand, the positiveness of g and η in the general equations (5), (34), and (36) is related to the positiveness of the thermal relaxation time τ in nonequilibrium energy formulas of EIT as well as in the Cattaneo equation of heat[13] where τ is proportional to g. It is easy to see from Eqs. (36) and (37) taken for $i=0$ that the positiveness of g, η, or τ constitutes the new nonclassical constraint that should be added to classical stability conditions of equilibrium, $c_V>0$ and $\chi>0$. Convection terms take into account the occurrence of the inverse process of macroscopic motion through fluctuations of the hydrodynamic velocity $\mathbf{u}$. The complete Legendre transformation of e, Eq. (34), yields in our one-component case the copotential

$$-\mu\equiv e^T=Ts-Pv+\mathbf{i}\cdot\mathbf{v}_s+\mathbf{u}^2-e \ , \tag{38}$$

which has to be expressed in terms of covariables $(T,P,\mathbf{v}_s,\mathbf{u})$. Transformed from the energy (34), this is the negative chemical potential, Eq. (10). It is equal to the partial derivative of the total energy with respect to mass when the total entropy, volume, and momenta are constant. However, in the multicomponent case $e^T=-\sum_i\mu_iy_i$, where y_i are mass fractions. Furthermore, $\sum_i\mu_iy_i$ is equal to the Gibbs free energy $G\equiv e+PV-Ts$ only if $\mathbf{u}\equiv\mathbf{i}\equiv\mathbf{0}$. In any system with more degrees of freedom than the classical ones the Gibbs free energy is no longer the sum of the products of the chemical potentials and masses (mole numbers) of the species. The appropriate property is exhibited in any case by the thermodynamic potential $-e^T$. Its perfect differential in our one-component case is

$$de^T=sdT-vdP+\mathbf{i}\cdot d\mathbf{v}_s+\mathbf{u}\cdot d\mathbf{u} \ . \tag{39}$$

The potential e^T is related to the classical Gibbs free energy G as follows:

$$-e^T=G-\mathbf{i}\cdot\mathbf{v}_s-\mathbf{u}^2 \ . \tag{38$'$}$$

Taking the equilibrium function $\mu^{\rm eq}$ of Eq. (10) in terms of $T^{\rm eq}$, $\rho^{\rm eq}$, expressing these variables in terms of nonequilibrium variables $T,P,\mathbf{v}_s,\mathbf{u}$ and performing a Taylor expansion to second order yields

$$-e^T\equiv\mu(T,P,\mathbf{v}_s,\mathbf{u})=\mu^{\rm eq}(T,P)-gs^2\mathbf{v}_s^2/2-\mathbf{u}^2/2 \ . \tag{40}$$

Indeed by differentiating (40), Eq. (39) is obtained as well as isothermal and isbaric nonequilibrium corrections to $s^{\rm eq}$ and $v^{\rm eq}$. The role of the (convex) function $\mathbf{u}^2/2-\mu^{\rm eq}$ is known in variational mechanics of perfect fluids.[6] The contravariant elements of the metric tensor are the elements of the Jacobian $\partial(s,v,\mathbf{i},\mathbf{u})/\partial(T,P,\mathbf{v}_s,\mathbf{u})$, the inverse of (36). The entropy version of these tensors[10] is of course $-T^{-1}$ times the corresponding elements of g_{ik} and g^{ik}. Using standard tensor transformations, $-\mathsf{g}_{ik}/T$ and $-\mathsf{g}^{ik}/T$ can be transformed to the natural variables of entropy $(e,v,\mathbf{i},\mathbf{u})$. Alternatively one can use Eq. (35) in the form

$$ds=T^{-1}de+(PT^{-1})dv-(\mathbf{v}_sT^{-1})\cdot d\mathbf{i}-(\mathbf{u}T^{-1})\cdot d\mathbf{u} \ , \tag{41}$$

and compute the Jacobians

$$\frac{\partial(T^{-1},PT^{-1},-\mathbf{v}_sT^{-1},-\mathbf{u}T^{-1})}{\partial(e,v,\mathbf{i},\mathbf{u})} \tag{42a}$$

and

$$\frac{\partial(e,v,\mathbf{i},\mathbf{u})}{\partial(T^{-1},PT^{-1},-\mathbf{v}_sT^{-1},-\mathbf{u}T^{-1})} \tag{42b}$$

to obtain the covariant and contravariant tensors.

For this purpose the function $s(e,v,i,u)$ describing the specific nonequilibrium entropy at point A, Fig. 1, should be evaluated from Eq. (34). Since the entropy s_A equals the equilibrium entropy at point B, the arguments of which are $e^{\rm eq}=e-\mathbf{u}^2/2-\mathbf{i}^2/(2gs^2)$ and $v^{\rm eq}=v$, then $s(e,v,\mathbf{i},\mathbf{u})\approx s^{\rm eq}(e-\mathbf{u}^2/2-\mathbf{i}^2/2gs^2,v)$ and after Taylor expansion

$$s(e,v,\mathbf{i},\mathbf{u})\approx s(e,v)-\mathbf{i}^2/[2Ts^2g(e,v)]-\mathbf{u}^2/2T(e,v) \ . \tag{43}$$

Here the equilibrium function $s(e,v)$ is expressed in terms of the nonequilibrium energy and volume of moving fluid which corresponds to taking the entropy $s^{\rm eq}$ at point C, Fig. 1. This entropy is greater than that at point B; the consequence of operating with this equilibrium function is that the kinetic terms divided by T have to be subtracted in Eq. (43) from $s(e,v)$ in order to obtain the true entropy of the system at point A.

The Legendre transform of s, Eq. (43), yields on the basis of (38) the coentropy

$$s^T(T^{-1},pT^{-1},-\mathbf{v}_sT^{-1},-\mathbf{u}T^{-1}) =-e^TT^{-1}=(\mu T^{-1})^{\rm eq}-T^{-1}gs^2\mathbf{v}_s^2/2-T^{-1}\mathbf{u}^2/2 \ . \tag{44}$$

Both s and s^T are concave functions around equilibrium. The ideal-gas result is the tensor generalizing that of Eq. (22) for $\mathbf{u}\neq\mathbf{0}$:

$$
g^{(s)}{}_{ik}=\begin{bmatrix}
-3k/2me^2-\dfrac{\beta_{ee}\mathbf{i}^2}{2} & \dfrac{-\beta_{\mathrm{ev}}\mathbf{i}^2}{2} & -\beta_e\mathbf{i}^\dagger & -T_e^{-1}\mathbf{u}^\dagger \\
\dfrac{-\beta_{\mathrm{ev}}\mathbf{i}^2}{2} & \dfrac{-k}{mv^2}-\dfrac{\beta_{\mathrm{vv}}\mathbf{i}^2}{2} & -\beta_v\mathbf{i}^\dagger & -T_v\mathbf{u}^\dagger \\
-\beta_e\mathbf{i} & -\beta_v\mathbf{i} & \dfrac{-15k^3[\underline{\mathbf{1}}]}{4m^3es^2} & [\underline{\mathbf{0}}] \\
-T_e^{-1}\mathbf{u} & -T_v^{-1}\mathbf{u} & [\underline{\mathbf{0}}] & \dfrac{-3k[\underline{\mathbf{1}}]}{2me}
\end{bmatrix}, \tag{45}
$$

where $15k^3/4m^3e=(Tg)^{-1}$ and $3k/2me=T^{-1}$. The planar space associated with the classical part of (45) is described in Ref. 24.

The Hessians of the entropy density ρ_s have proven suitable to investigate the stability problems of thermohydrodynamic equations of change for energy, mass, and momentum in which the density arguments $E\equiv\rho e$, $\rho\mathbf{u}^2/2$, and $\rho\mathbf{u}$ appear in a natural manner.[15] From Eq. (5)

$$
\begin{aligned}
\rho_s=S_v(E,\rho,\mathbf{I},\mathbf{J})&\approx S_v(E-g^{-1}\rho\rho_s^{-2}\mathbf{I}^2/2-\rho^{-1}\mathbf{J}^2/2,\rho)\\
&\approx S_v(E,\rho)-g^{-1}\rho\rho_s^{-2}\mathbf{I}^2/(2T)\\
&\quad-\rho^{-1}\mathbf{J}^2/(2T)\ ,
\end{aligned} \tag{46}
$$

and the perfect differential of ρ_s is

$$
d\rho_s=T^{-1}dE-(\mu T^{-1})d\rho-T^{-1}\mathbf{v}_s\cdot d\mathbf{I}-T^{-1}\mathbf{u}\cdot d\mathbf{J}\ . \tag{47}
$$

Now we specialize with an example. The covariant tensor[25]

$$
g_{ik}^{(s)}=\frac{\partial(T^{-1},\mu T^{-1},\mathbf{v}_sT^{-1},\mathbf{u}T^{-1})}{\partial(E,\rho,\mathbf{I},\mathbf{J})} \tag{48}
$$

for the ideal gas, for which

$$
\beta\equiv(gTs^2)^{-1},\quad \beta\rho_{ee}^{-1}=\frac{\partial^2\beta\rho^{-1}}{\partial E^2},\quad \beta_{e\rho}=\frac{\partial^2\beta\rho^{-1}}{\partial E\partial\rho}
$$

is

$$
g_{ik}^{(s)}=\begin{bmatrix}
\dfrac{-3k\rho}{2mE^2}-(\rho^{-1}\beta)_{\mathrm{ee}}\dfrac{\mathbf{I}^2}{2}-(\rho T)_{ee}^{-1}\dfrac{\mathbf{J}^2}{2} & (3k/2mE)-(\rho^{-1}\beta)e\rho\dfrac{\mathbf{I}^2}{2}-(\rho T)_{e\rho}{}^{-1}\dfrac{\mathbf{J}^2}{2} & -(\rho^{-1}\beta)_e\mathbf{I}^\dagger & -(\rho T)_e^{-1}\mathbf{J}^\dagger \\
3k/2mE-(\rho^{-1}\beta)_{e\rho}\dfrac{\mathbf{I}^2}{2}-(\rho T)_{e\rho}{}^{-1}\mathbf{J}^2/2 & -5k/2m\rho-(\rho^{-1}\beta)_{\rho\rho}\dfrac{\mathbf{I}^2}{2}-(\rho T)_{\rho\rho}^{-1}\dfrac{\mathbf{J}^2}{2} & -(\rho^{-1}\beta)_\rho\mathbf{I}^\dagger & -(\rho T)_\rho^{-1}\mathbf{J}^\dagger \\
-(\rho^{-1}\beta)_e\mathbf{I} & -(\rho^{-1}\beta)_\rho\mathbf{I} & -(\rho^{-1}\beta)[\underline{\mathbf{1}}] & [\underline{\mathbf{0}}] \\
-(\rho T)_e^{-1}\mathbf{J} & -(\rho T)_\rho^{-1}\mathbf{J} & [\underline{\mathbf{0}}] & -(\rho T)^{-1}[\underline{\mathbf{1}}]
\end{bmatrix}. \tag{49}
$$

(The flux corrections are written in the form usual for both ideal gas and nonideal fluid.) The negativity of the determinant of this tensor and its principal minors at equilibrium ($\mathbf{u}=\mathbf{v}_s=\mathbf{0}$) constitute the stability conditions for the fluid with fluctuations in its velocity, heat flux, density, and energy. [See Eq. (69), below, for other statements of equilibrium conditions.] The perfect differential of the energy of unit volume $E=\rho e(\rho_s,\rho,\mathbf{I},\mathbf{J})$, Eq. (5), is

$$
dE=Td\rho_s+\mu d\rho+\mathbf{v}_s\cdot d\mathbf{i}+\mathbf{u}\cdot d\mathbf{J}\ . \tag{50}
$$

Using Eqs. (5), (9), (10), and (50) in the expression for the second differential of entropy density associated with Eq. (47) one obtains

$$
\begin{aligned}
\delta^2(\rho s)&=[\delta T^{-1}\delta E-\delta(\mu T^{-1})\delta\rho-\delta(\mathbf{v}_sT)^{-1}\cdot\delta\mathbf{I}-\delta(\mathbf{u}T^{-1})\cdot\delta\mathbf{J}]\\
&=\{[\delta T^{-1}\delta\rho_e-\delta(\mu T^{-1})\delta\rho]^{\mathrm{eq}}_{u=0,v_s=0}-T^{-1}\delta\mathbf{v}_s\cdot\delta\mathbf{I}-T^{-1}\delta\mathbf{u}\cdot\delta\mathbf{J}\}\\
&=\delta^2[(\delta s)^{\mathrm{eq}}_{u=0,v_s=0}-\mathbf{I}^2/(2gs^2\rho T)-\mathbf{J}^2/\rho T]=\rho\delta^2[s^{\mathrm{eq}}_{u=0,v_s=0}-\mathbf{i}^2/(2gs^2T)-\mathbf{u}^2/(2T)]\ ,
\end{aligned} \tag{51}
$$

where ρ_e is the density of the equilibrium *internal* energy. One may see an interaction of equilibrium and flow terms in (51). When $\mathbf{I}=\mathbf{q}=\mathbf{0}$ and $\mathbf{J}=\mathbf{0}$, Eqs. (49) and (51) simplify to the well-known equilibrium results.[15,17] The dual of ρ_s is the density of the (nonequilibrium) grand potential $(-P/T)$ and for small $\mathbf{u}$ and $\mathbf{v}_s$ this dual is

$(\Pi\equiv-P/T)$

$$
\begin{aligned}
&\Pi(T^{-1},\mu T^{-1},\mathbf{v}_sT^{-1},\mathbf{u}T^{-1})\\
&\qquad\approx\Pi^{\mathrm{eq}}(T^{-1},\mu T^{-1})-T^{-1}\rho gs^2\mathbf{v}_s^2/2-T^{-1}\rho\mathbf{u}^2/2\ .
\end{aligned} \tag{52}
$$

The quadratic form associated with Eqs. (49) and (51) and small perturbations of E, ρ, $\mathbf{I}$, and $\mathbf{J}$ can be accepted as a Liapunov function to investigate the stability problems involving fluid motion and heat transfer. As was stressed by Glansdorff and Prigogine,[15] the hydrodynamic problem can be handled by using the so-called $\delta^2 z$ criterion where $z = s - \mathbf{u}^2/2T$ instead of the conventional $\delta^2 s$ criterion. Our Eqs. (46), (49), and (51) show how to define ρ_z and its second differential in the case involving heat transfer and convection and prove that Z is nothing but S expressed in appropriate variables which take into account role of momentum-related terms; see also Oono.[20]

The dual of E of Eq. (50) is $E^T \equiv -\Omega$, corresponding to the intensities (9) and (10) as well as velocities $\mathbf{v}_s$ and $\mathbf{u}$. Its perfect differential is

$$dE^T \equiv -d\Omega = \rho_s dT + \rho d\mu + \mathbf{I}\cdot d\mathbf{v}_s + \mathbf{J}\cdot d\mathbf{u} \ . \tag{53}$$

For our energy E, Eq. (5), the complete Legendre transformation leads to the nonequilibrium pressure function, Eq. (12), in the form

$$-\Omega \equiv P = P^{\rm eq}(\rho_s,\rho) - \frac{1}{2}\left[\frac{\partial g}{\partial \rho}\right]_s \left[\frac{\mathbf{q}}{T}\right]^2 , \tag{12$'$}$$

which was discussed comprehensively in Ref. 1. When expressed in terms of its natural variables T, μ, v_s, and u, this pressure function becomes

$$-\Omega \equiv E^T = P^{\rm eq}(\hat{T},\hat{\mu}) - g_\rho \rho_s^2 \mathbf{v}_s^2/2 \ , \tag{54}$$

where

$$\hat{T} = T + gs\mathbf{v}_s^2 + \left[\frac{\partial g}{\partial s}\right] s^2 \frac{\mathbf{v}_s^2}{2} \ ,$$

and

$$\hat{\mu} = \mu + \frac{\mathbf{u}^2}{2} = \tfrac{1}{2} g s^2 \mathbf{v}_s^2 \left[1 - \left[\frac{\partial \ln g}{\partial \ln \rho}\right]_s + \left[\frac{\partial \ln g}{\partial \ln s}\right]_\rho \right] .$$

Here the complicated arguments of $P^{\rm eq}$ are the equilibrium temperature and chemical potential expressed in terms of T, μ, $\mathbf{v}_s$, and $\mathbf{u}$. Taylor expansion yields the potential

$$-\Omega(T,\mu,\mathbf{v}_s,\mathbf{u}) \approx P^{\rm eq}(T,\mu) + \rho\mathbf{u}^2/2 + \rho_s g s \mathbf{v}_s^2/2 \ , \tag{55}$$

which contains the same kinetic corrections as E, convex around equilibrium. Differentiating (55) leads to (53) if the nonequilibrium corrections are made, pertaining now to ρ_s and ρ. The covariant tensor

$$g_{ik} = \frac{\partial(T,\mu,\mathbf{v}_s,\mathbf{u})}{\partial(\rho_s,\rho,\mathbf{I},\mathbf{J})} \tag{56}$$

contains the nonequilibrium corrections through the nonequilibrium temperature and chemical potential which do not disappear even for the ideal gas ($g =$const). The tensor (56) has the structure

$$\mathsf{g}_{ik} = \begin{bmatrix} \dfrac{\partial T}{\partial \rho_s} & \dfrac{\partial T}{\partial \rho} & -2\rho_s^{-1}\mathbf{v}_s^\dagger & \mathbf{0}^\dagger \\ \dfrac{\partial \mu}{\partial \rho_s} & \dfrac{\partial \mu}{\partial \rho} & (\rho_s^2 g)^{-1}\mathbf{I}^\dagger & -\rho^{-1}\mathbf{u}^\dagger \\ -2\rho_s^{-1}\mathbf{v}_s & (\rho_s^2 g)^{-1}\mathbf{I} & (\rho_s g s)^{-1}[\underline{\mathbf{1}}] & [\underline{\mathbf{0}}] \\ \mathbf{0} & -\rho^{-1}\mathbf{u} & [\underline{\mathbf{0}}] & \rho^{-1}[\underline{\mathbf{1}}] \end{bmatrix} , \tag{57}$$

and the inverse of Eq. (57) is the pressure function tensor. The upper left 2×2 block is the classical part. Coupling with the velocity field is due to presence of ρ in the kinetic energy of unit volume $\rho\mathbf{u}^2/2$. The g terms describe the role of heat flux. Although (57) and (49) are conformally equivalent,[11] it is easy to see that the energy tensor of the ideal gas in the frame of its natural variables is simpler than the corresponding entropy tensor.

It may be proved even classically[26] that if mass diffusion takes place in the system, then the corresponding term in the Gibbs equation for the *specific* energy differential is of the form $\mathbf{v}_k \cdot d(\rho^{-1}\rho_k \mathbf{v}_k)$ for species k, where $\mathbf{v}_k$ is the momentum of diffusion of the species k in the fluid frame, i.e., the difference between the laboratory-frame velocity of this species, $\mathbf{u}_k$, and the velocity of convection $\mathbf{u}$. [The corresponding contribution to the energy of unit volume is the term $\mathbf{v}_k \cdot d(\rho_k \mathbf{v}_k)$.] Since this is the same formal structure as in Eq. (35) where the term $\mathbf{v}_s \cdot d\mathbf{i} = \mathbf{v}_s d(\rho^{-1}\rho_s \mathbf{i}_s)$ pertains to the entropy transfer, it is not difficult to extend the present theory to treat mass diffusion in multicomponent systems. The Gibbs equation for the multicomponent system of course contains the sum of the contributions from both diffusional and thermal momenta.

VI. THERMOHYDRODYNAMIC STABILITY AROUND EQUILIBRIUM IN THE EXTENDED STATE SPACE

Let us apply the first expression on the right-hand side of Eq. (51) to determine the stability conditions for transients around equilibrium. Consider a physical system contained within a fixed volume $\tilde{V}$ wherein the fluctuations of the densities of energy, heat, and momenta may occur. Working in the framework of the Liapunov theory[15,27,28] we evaluate the time derivative of the second differential of the total entropy [$\delta\dot{E} \equiv \partial(\delta E)/\partial t$, etc.; note the interchangeability of the operators δ and $\partial/\partial t$]

$$\begin{aligned} \tfrac{1}{2}(\delta^2 \dot{S})_{\rm (total)} = \int\!\!\int\!\!\int [& \delta T^{-1}\delta\dot{E} - \delta\mu T^{-1}\delta\dot{\rho} \\ & - \delta\mathbf{v}_s T^{-1}\cdot\delta\dot{\mathbf{I}} \\ & - \delta\mathbf{u} T^{-1}\cdot\delta\dot{\mathbf{J}}] d\tilde{V} \ . \end{aligned} \tag{58}$$

The conservation and evolution equations pertaining to the Lagrangian (1) consistent with Eq. (58) were derived in Ref. 1. Their perturbed form, which should be substituted to Eq. (58), is

$$\delta\dot{E} = -\nabla\cdot\delta(\rho\mathbf{u}E + P\mathbf{u} + \mathbf{q} + \mathbf{\Pi}_s\cdot\mathbf{u}_s) \quad \text{(energy conservation)}\,, \tag{59}$$

$$\delta\dot{\rho} = -\nabla\cdot\delta\mathbf{J} \quad \text{(mass conservation)}\,, \tag{60}$$

$$\delta\dot{\mathbf{J}} = -\nabla\cdot\delta(\rho^{-1}\mathbf{J}\mathbf{J} + \mathbf{1}P + \mathbf{\Pi}_s) \quad \text{(momentum conservation)}\,, \tag{61}$$

$$g(\rho T)^{-1}\delta\dot{\mathbf{q}} = -\nabla\delta T - \lambda^{-1}\delta\mathbf{q} \quad \text{(heat conduction)}\,, \tag{62}$$

$$\delta\mathbf{\Pi}_s = -2\eta_s\nabla\delta\mathbf{v}_s \quad \text{(viscosity equation)}\,. \tag{63}$$

Fixed boundary conditions are assumed which exclude any fluctuations of any independent variable on the surface $\tilde{A}$ surrounding the volume $\tilde{V}$. The coefficients in Eqs. (58)–(63) are evaluated at the equilibrium state, point C, Fig. 1, and are kept constant (linear stability). Bulk viscosity effects are neglected.[1] Since any elastic effects are neglected in Eq. (1), Eq. (63) for the shear viscosity has the form of Newton's law. On the other hand, the heat Eq. (62) has Cattaneo structure[1,13] due to the inertial (g) term in Eq. (1). The standard approach developed in Ref. 15 is used to transform the terms such as $\delta\mu T^{-1}\delta\dot{\rho} = -\delta\mu T^{-1}\nabla\cdot\delta\mathbf{J}$ into the divergences $\nabla\cdot(\delta\mu T^{-1}\delta\mathbf{J})$ and remainders, so one can apply Gauss's theorem yielding the surface integral with the products $\delta\mu T^{-1}\delta\mathbf{J}$, etc. Neglecting this integral (it vanishes on the surface $\tilde{A}$ where no perturbations are allowed) and using the extended Gibbs-Duhem equation resulting from the Legendre transform of Eq. (47)

$$E\delta T^{-1} + \delta p T^{-1} - \rho\delta(\mu T^{-1}) - \mathbf{I}\cdot\delta(\mathbf{v}_s T^{-1}) - \mathbf{J}\cdot\delta(\mathbf{u}T^{-1}) = 0\,, \tag{64}$$

we obtain

$$\tfrac{1}{2}\delta^2\dot{S}^{\text{eq}}_{\text{total}} = \int\int\int[(\delta\mathbf{q}\cdot\delta\mathbf{q}/\lambda T^2) + (\delta\mathbf{\Pi}_s:\delta\mathbf{\Pi}_s/2\eta_s T)]d\tilde{V}\,. \tag{65}$$

According to the Liapunov theorem the sufficient stability conditions for $\delta^2 S_{(\text{total})}$ taken as the Liapunov functional are

$$\delta^2 S_{\text{tot}} < 0 \tag{66}$$

and

$$\delta^2\dot{S}_{\text{tot}} > 0\,. \tag{67}$$

From Eqs. (65) and (67) one can conclude the positivity of the transport coefficients

$$\lambda > 0, \quad \eta_s > 0 \tag{68}$$

and, from Eq. (66) by using the equilibrium form of Eq. (49) or of any thermodynamic tensor derived in this work,

$$C_v > 0, \quad \chi_T \equiv -\left[\frac{\partial P}{\partial \ln V}\right]_T > 0\,, \quad g > 0, \quad \rho > 0, \quad T > 0\,. \tag{69}$$

Around equilibrium, the inequalities (68) are simply the consequence of the second law represented by Eqs. (65) and (67). The inequalities (69) are the concavity conditions for the equilibrium Gibbs surface representing the entropy in the extended space $E,\rho,\mathbf{I},\mathbf{J}$. The conditions $g > 0$ and $\eta_s > 0$ are new. The first one indicates that the heat flux contribution to the extended entropy function can be only negative (and the energy, positive), i.e., the presence of heat should increase the organization of the system around the equilibrium. The second condition requires that the viscosity phenomena associated with heat flow (first revealed by Grad[8]) should be characterized by a positive coefficient of viscosity η_s.

As indicated by the form of the metric tensors obtained in this work around nonequilibrium states g_{ik} (and hence $\delta^2 S$) can be of indefinite sign since they contain mixed (flow) terms linear with respect to $\mathbf{I}$ and $\mathbf{J}$. The properties of the stable Gibbs surface contained in (69) are in this case not enough to define the stability conditions of any nonequilibrium manifold. One can, however, rely on $\delta^2 S$ exclusively to obtain nonequilibrium counterpart of the conditions (69) provided that one is able to prove additionally that the final derivative $\delta^2\dot{S}$ keeps definite sign within the volume investigated. In a future work we will apply this formalism to a thermodynamic analysis of turbulence.

VII. CONCLUSIONS

The following are the conclusions drawn from this paper.

(a) The problem of nonequilibrium thermodynamic length has been stated phenomenologically based on EIT. Thermodynamic metric tensors are given for a flowing fluid with heat flow in field representation which includes variables—degrees of freedom—to represent the degree of disequilibrium. With these variables, it is possible to achieve the invariant form[12] of the Einstein formula for the probability of fluctuations around equilibrium, by taking into account the fluctuations of the macroscopic motion and heat flux. This is associated with inclusion of momenta (or velocity terms) into our thermodynamic field formalism, which differs at this point from the traditional one. However, once stated, the near-equilibrium stability conditions of a moving nonequilibrium fluid with heat are automatically contained in the positive-definite character of the energy-representation tensors at $u = v_s = 0$ or the negative-definite character of the entropy representation tensors and no new criteria such as that for $\delta^2 Z$ are needed. This is due to the fact that the inequality $\partial(\delta^2 S)/\partial t > 0$ always holds at equilibrium as a consequence of the second law.

(b) It was shown that the physical nature of the thermodynamic potentials that define the metric and corresponding criteria of stable equilibrium remains unchanged when the convection and nonequilibrium (heat) phenomena are taken into account. Concavity or convexity at equilibrium is preserved provided that, besides the classical conditions $C_v > 0$ and $\chi > 0$, the inertial coefficients in the extended energy formulas are positive, i.e., inequalities (69) hold. The second differentials of the energy, entropy, and their corresponding copotentials are still applicable as the Liapunov criteria[28] to be tested for nonequilibrium fluctuations. In particular $\delta^2 Z$ of Glansdorff and Prigogine is just $\delta^2 S$ expressed correctly in terms of the total energy and momentum variables allowing mechanical degrees of freedom. This agrees with the conclusion Oono[21] obtained for the case neglecting the heat. Since, however, the sign of $\partial(\delta^2 \rho S)/\partial t$ out of equilibrium is in general indefinite, the extended thermodynamic potentials and tensors derived here are not capable of providing the complete set of the stability conditions out of equilibrium, unless one proves additionally that $\partial(\delta^2 \rho S)/\partial t$ is of definite sign within the volume investigated.

(c) The following simple rule is helpful to adjust properly the sign of the nonequilibrium and convection terms in the nonequilibrium thermodynamic potentials: kinetic terms pertaining to macroscopic motion and heat flow should be added to the convex equilibrium functions or subtracted from the concave equilibrium functions of energy type. In entropy-type functions the same rule holds for the sum of the kinetic quantities divided by the temperature. However, the arguments of the equilibrium functions in question must always be the total nonequilibrium quantities pertaining to the real state of the fluid; see Eq. (55).

(d) The inclusion of mass diffusion terms conforms to the same formalism (see the end of Sec. V).

(e) To preserve positive (definite-sign) metrics, only those of thermodynamic potentials were considered which, at equilibrium, are convex or concave with respect to either static- or kinetic-type variables. There is no evidence that geodesic lines for such metrics should be associated with a natural motion (e.g., fluctuation decay) in the system; perhaps indefinite-sign metrics corresponding to the Lagrangian,[7] with the sign of kinetic terms reversed, would be competitive candidates in this regard.

(f) The approach presented here is valid only close to equilibrium. Other results from work in progress, which will be communicated soon, indicate that the thermodynamics of systems further from equilibrium must be nonlocal and that some additional state variables need to be added to those introduced here.

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