

Least-entropy generation: Variational principle of Onsager's type for transient hyperbolic heat and mass transfer

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For coupled transfer of the energy and mass in a multicomponent system at mechanical equilibrium a simple thermodynamic theory is developed, and the damped wave equations of change are derived. We show that under nonstationary conditions, where relaxation of diffusive fluxes is essential, the evolution of the distributed coupled transfer of the energy and mass follows the path that minimizes the difference between the total entropy generated within the system and that exchanged by the system. The principle is also valid in the limit in which flux relaxation effects are negligible and the heat and mass transfer, whether steady or not, obeys Onsager's generalization of the Fourier and Fick laws. For coupled steady-state processes the principle goes into that of Onsager, yielding his phenomenological equations. In contrast to the local steady-state nature of Onsager's principle the new principle is global, valid for both stationary and transient situations, and requires no frozen fields. For an isolated, distributed system, in which transient relaxation to equilibrium is the only possible process, the principle implies the least possible increase of the system entropy between any two successive configurations.

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I. INTRODUCTION

The problem of the wave terms in the equations of change for the energy, mass, and momentum has recently attracted the attention of many researchers, and even comprehensive reviews are available [1–3]. Notwithstanding, the question of couplings among the vector transport processes is attacked rather seldom in that context [4,5]. The typical working expression for the nonequilibrium entropy or energy used in the extended irreversible thermodynamics (EIT) [2] contains only scalar relaxation terms which limit the applicability of treatments based on these couplings. Such couplings are, however, very important in any process with simultaneous heat and mass transfer. This motivates the present work in which the set of coupled-wave equations is derived from irreversible thermodynamics and the underlying variational principle of Onsager's type is formulated.

The conventional constitutive equations of Fourier and Fick relate irreversible diffusional fluxes of heat and mass, respectively, to gradients of temperature and concentration. Combining these with conservation laws leads to parabolic equations of change. However, all standard equations with parabolic terms have a nonphysical property: a disturbance at any point in the medium is felt instantly at every other point; that is, the velocity of propagation of disturbances is infinite. This paradox is clear in certain routine solutions of parabolic equations [6]. An example [7] is the case of heat conduction in a semi-infinite solid whose surface temperature may suddenly increase from $T=0$ to a constant nonzero T_{surf} . The solution [8], which is expressed in terms of the error integral, provides $T=0$ at the time $t=0$, but for any arbitrarily short time t and arbitrarily large distance x from the wall, the temperature $T(x,t)$ is nonvanishing, imply-

ing infinitely fast propagation of the disturbance.

Such nonphysical behavior has been pointed out by many authors; among them [8–15] the dilemma was first resolved by the acceptance of the hypothesis of heat flux relaxation. This hypothesis was elevated to the rank of theory on the basis of many works in nonequilibrium statistical mechanics, theory of heat conduction, and the so-called extended irreversible thermodynamics. Solid justification was obtained from Grad's solution of the Boltzmann kinetic equation [15], applied either in the context of phenomenological equations [2,14], or conservation laws [16,17]. Relativistic theories also appeared [18,19]. Experiments confirming the wave nature of heat are available [20–22]. In the solid-state community an opinion is frequently held that use of wave theory is necessary in the so-called "ballistic" regime of phonon transfer, which is in fact the wave regime [23–25], and that failure to appreciate this fact has led to a number of invalid statements about the heat transfer in solids. Experiments in acoustic absorption and dispersion [26] and Domanski's analysis [27] of the thermal behavior of solids heated by laser pulses showed the superiority of the generalized (wave-type) of Navier-Stokes equation and Fourier heat equation over their classical counterparts, particularly in the high-frequency regimes. Extended thermodynamic theories justifying the unsteady relaxation terms in terms of the extended, flux-dependent entropy are available [1,2,28].

Here we work out a simple thermodynamic account of vector couplings occurring during the simultaneous heat and mass transfer. Then we formulate a variational principle, of Onsager type, which yields a complete set of equations describing *hyperbolic* heat and mass transfer. The principle is physical insofar as it shows that, from a reference internal to the system, any coupled heat and

mass transfer process subject to conservation constraints evolves so that the growth of the total entropy generated is as low as possible. By “a reference internal to the system” we mean what is described by the partial-differential equations of the process, regardless of its boundary conditions. The principle is of general interest in view of persistent doubts regarding the existence of exact (i.e., of unconstrained type) variational principles for irreversible phenomena [29–34].

While hyperbolic rather than parabolic equations are the main interest of this paper, the principle applies equally well to the limiting case of infinite propagation speed, when the system becomes parabolic, thus including the standard description. The resulting equation set is composed of the phenomenological equations, conservation laws, and the equations of change for the densities and fluxes.

The main virtue of the principle is its physical implication: the difference between the entropy generated within the dissipative system and the entropy exchanged by this system is as small as possible. This is valid in both unsteady and steady situations. For an isolated system this simply means the least possible generation of the entropy within the system. For steady-state processes the principle implies the least possible entropy output for any input constant in time. It then goes over into the well-known Onsagerian principle which yields the phenomenological equations by minimizing the difference between the flux-based dissipation function and the bilinear expression for the entropy production. However, Onsager’s principle is local and is valid only for steady states. It is also of the quasivariational type in the sense that it holds so long as the thermodynamic forces are kept frozen. For local quasivariational principles the freezing of the thermodynamic forces can be relaxed [35], but it persists in nearly all global unsteady-state formulations known so far [e.g., 31,35]. Exceptional in this regard is the collection of the global principles involving the Lagrangians containing the time explicitly [36], not requiring, in principle, any frozen fields. However, there are serious difficulties in interpreting these Lagrangians as the physical quantities due to the strange behavior of the related Hamiltonians [37] and difficulties persist in applying them to any complex (multivariable) dissipative systems where various degrees of freedom are coupled [38].

The present principle is global, it is valid for both stationary and transient situations, and it does admit variations of all physical fields present in the system. The point crucial for this successful formulation is that the principle involves a four-dimensional functional over a region in space-time, and not the three-dimensional functionals over space only, considered in earlier works. The functional is the properly expressed change of entropy, given in terms of the two dissipation functions. By requiring the least increase of the entropy in any isolated system (during a transient relaxation to equilibrium) between any two successive configurations, the principle shows that the entropy plays a role in thermodynamics similar to that of the action in mechanics. The main practical value of the principle lies in that it allows for derivation of the equations of change in a systematic way

under the given dissipation functions and the well-known information contained in the conservation laws. It is demonstrated here for the coupled-wave heat and mass transfer in Galilean (nonrelativistic) frames.

Through the whole work the macroscopic motion of a multicomponent system is taken into account in the simplest possible manner, as the motion of the system in mechanical equilibrium. This is a frequent and convenient assumption which allows us to single out heat and mass transfer processes from the total thermohydrodynamic behavior. In this case the hydrodynamic velocity \mathbf{v} , total mass density ρ , and the pressure P are the constant parameters rather than the state variables, which is consistent only with uniform motion of the macroscopic system. Applications to other processes (e.g., hydrodynamics, chemical kinetics, etc.) will be reported.

For brevity, we use throughout the first and the second substantial derivative operators, $d/dt = \partial/\partial t + \mathbf{v} \cdot \text{grad}$, and $d^2/dt^2 = d/dt (d/dt)$, respectively. In the absence of macroscopic motion ($\mathbf{v} = \mathbf{0}$) these substantial derivatives simplify to the corresponding partial derivatives. For the vector sets and matrices characterizing multicomponent systems we use the notation of de Groot and Mazur [39]. Multicomponent systems composed of n species are described by the flux vector \mathbf{J} , Eq. (10), composed of $n - 1$ independent diffusive fluxes of mass $\mathbf{J}_1, \mathbf{J}_2, \dots, \mathbf{J}_{n-1}$ and the energy flux \mathbf{J}_q . Since the sum of all the diffusive fluxes of mass vanish, the n th mass flux results as the negative of the sum $\mathbf{J}_1 + \mathbf{J}_2 + \dots + \mathbf{J}_{n-2} + \mathbf{J}_{n-1}$. Similarly, the system state is defined by the vector \mathbf{z} of $n - 1$ independent mass fractions y_1, y_2, \dots, y_{n-1} , and the specific enthalpy h , Eq. (9). The n th mass fraction results from the condition that the sum of all n mass fractions equals unity. Consequently, in the matrix formalism of Sec. III, all n th components refer to the energy properties rather than those of the n th mass component.

II. RELAXATION OF PURE HEAT FLUX

Since some information about uncoupled relaxation processes is in order first, we begin with pure heat transfer in an isobaric, single-component system moving with a constant velocity \mathbf{v} . The relaxation theory is based on the supposition that Fourier’s, Fick’s, and Newton’s laws are asymptotic approximations to a more exact equation, the Maxwell-Cattaneo equation,

$$\mathbf{J}_h = -\lambda \nabla T - \tau_h \frac{d\mathbf{J}_h}{dt}, \quad (1)$$

where τ_h is the relaxation time of heat flux. The analogous equations for the irreversible fluxes of mass and momentum have also been found. For mass diffusion an equation identical with Eq. (1) results from the nonstationary version of the Maxwell-Stefan equation under certain broad conditions [40].

Combining Eq. (1) with the simplest conservation law for the classical thermal energy leads to an equation of change,

$$\rho C_p \frac{dT}{dt} = \lambda \left[\nabla^2 T - \frac{d^2 T}{c_0^2 dt^2} \right], \quad (2)$$

where

$$c_0 = \sqrt{a_h / \tau_h} = \sqrt{\lambda / (\rho C_p \tau_h)} \quad (3)$$

is called the propagation speed of the thermal wave. When c_0 approaches infinity, Eq. (2) simplifies to the well-known parabolic equation of heat. On the other hand, Eq. (2) is of hyperbolic type and its solution [7,41] for the above-mentioned case of heating of a semi-infinite solid has this realistic property: two regions exist in a solid; the first in which the heat transfer has already taken place (disturbed region), and the second where the disturbance is not yet present (undisturbed region). The temperature $T(x,t)$ has a jump at the distance $x = c_0 t$ from the source of heat placed at $x = 0$ (heating of solid by a fluid). In contrast, as mentioned above, Fourier theory predicts the appearance of the disturbances everywhere, even for distances x_c greater than ct , where c is the light speed, which is of course unphysical behavior.

According to the hyperbolic model the wall heat flux $J_h(x=0)$ does not start instantaneously, but rather grows gradually [7] with a rate which depends on the relaxation time τ_h . After some time the wall heat flux reaches a maximum and then decreases, similar to the Fourier case. This decrease is a classical effect, occurring because the temperature gradient at the wall decreases in the course of heating of the solid. The Fourier and Fick theories are inappropriate for description of short-time effects [42] and high-frequency transfer. Furthermore, although relaxation times are typically very small, such effects can still have theoretical and practical importance. The absolute value of the relaxation time itself is by no means an appropriate criterion to judge whether or not the relaxation terms should be taken into account. Rather the product of this time and a characteristic frequency (the reciprocal of a time constant), describing the transient renewal in the system, is the relevant criterion. Usually one assumes that the flux relaxation terms are essential when the frequency of the fast variable transients is comparable (or greater) to the reciprocal of a longest relaxation time of the process.

The relaxation times τ for heat, mass diffusion, and momentum differ. They are designated here with the subscripts h , d , and m , respectively. At normal conditions the heat relaxation times are of the order of $\tau_h = 10^{-9}$ s for gases, and 10^{-12} s for liquids and metals. Relaxation times can be much greater in rarefied gases, viscoelastic liquids, capillary porous bodies, dispersed systems, Brownian systems, and superfluid helium; for capillary porous bodies, for example, Luikov evaluated effective $\tau_d = 10^{-4}$ s [43]. Brownian diffusion in the diameter range 10^{-7} – 10^{-3} m is characterized by times from $\tau_d = 3 \times 10^{-8}$ to 3 s [44]. These evaluations were based on use of some experimental data [45] and the experimentally confirmed Stokes term of the equation of motion. For liquid helium: $\tau_h = 4.7 \times 10^{-3}$ s [22–24,46,47]. Regarding momentum relaxation, which is ignored here, we refer the reader to the literature

[26,42,48–50].

It is both theoretically interesting and practically useful to know that propagation speeds for the disturbances of the energy, momentum, and mass are similar. For the ideal gas their equality is a theorem of kinetic theory. They all are equal to the propagation speed of the shear waves $(G/\rho)^{1/2}$, where G is the shear modulus, equal to the pressure P for the ideal gas. The common value of $c_0 = (G/\rho)^{1/2}$ can be interpreted as a consequence of the unity of the transfer phenomena occurring in a thermal wave front [51–54] and it is a suitable approximate hypothesis for starting a general treatment. For the ideal gas,

$$c_h \equiv \sqrt{D_h / \tau_h} = c_d \equiv \sqrt{D_d / \tau_d} = c_m \equiv \sqrt{\nu / \tau_m} = \sqrt{P / \rho}. \quad (4)$$

Here ν is the kinematic viscosity or the diffusivity of the momentum. Hence one can compute the relaxation times of an ideal gas as

$$\tau_h = \frac{\rho D_h}{P}, \quad \tau_d = \frac{\rho D_d}{P}, \quad \tau_m = \frac{\rho \nu}{P} = \frac{\eta}{P}, \quad (5)$$

where η is the dynamic viscosity. For ideal liquids the shear modulus G appears instead of pressure in the formulas (4) and (5). Hence the common propagation speed of ideal fluids is

$$c_0 = \sqrt{G / \rho}. \quad (6)$$

III. THERMODYNAMICS OF COUPLED HEAT AND MASS TRANSFER

Consider now a multicomponent system with simultaneous heat and mass transfer. Again, the system can move with a uniform velocity. The basic nonstationary equation of diffusive transport of matter, the Maxwell-Stefan equation of diffusion, leads to the unsteady relaxation terms in the phenomenological equations [40]. Below we will show that these relaxation terms are justified by irreversible thermodynamics. However, the classical expressions for entropy and entropy sources do not apply in the present (relaxation) case because the flux relaxation phenomenon is a consequence of local nonequilibrium in the macroscopic medium. Both phenomenological [55] and statistical approaches [2,14,16], the latter based on Enskog and Grad's iteration methods, lead to the conclusion that the entropy of a medium not in local equilibrium differs from the static (i.e., equilibrium) entropy, and the difference depends on all diffusive fluxes $\mathbf{J}_1, \mathbf{J}_2, \dots, \mathbf{J}_{n-1}, \mathbf{J}_q$. Evaluating this (negative) excess entropy is the objective of the so-called extended irreversible thermodynamics [1,2,5,16,17,28,55–64], and of many other formulations of irreversible thermodynamics. Despite differences in various approaches, the basic procedure can be characterized by the representative scheme outlined below, the simplest possible. (Again, for brevity, we ignore the momentum diffusion and any possible nonuniformity of the macroscopic motion. The latter simplification allows the constant density assumption.)

The difference between the true local entropy of a

nonequilibrium state s and the thermostatic entropy s^{eq} , which Onsager called the "kinetic entropy" or the "flux entropy," is associated with the tendency of every element of a continuum to recover thermodynamic equilibrium during the relaxation of diffusive fluxes of heat and mass; when the fluxes \mathbf{J} tend to zero, the entropy density goes to a maximum s^{eq} . Since any relaxation is an irreversible process the flux entropy $s-s^{eq}$, defined with respect to a stable local equilibrium, is always negative, a consequence of the concavity of the entropy around any macroscopically stable equilibrium.

The flux entropy is in fact ill defined unless either the equilibrium reference state or the relaxation path is specified. This is because the definition of a nonequilibrium state carries with it an infinity of possible equilibrium states to which the system can relax, depending on constraints. The ambiguity associated with the reference has led, on occasion, to apparent paradoxes and inconsistencies [16,17]. Due to constancy of P , \mathbf{v} , and ρ in the uniform flow, the definition of the flux entropy used here corresponds to the reference state of both constant energy or enthalpy, in the entropy picture of thermodynamics.

The contribution of flux entropy in the total nonequilibrium entropy expression is expressed by the last term in the formula

$$ds = T^{-1}de + PT^{-1}d\rho^{-1} + \sum_1^{n-1} (\mu_n - \mu_i)T^{-1}dy_i - \sum_1^n \sum_1^n \gamma_{ik} \mathbf{J}_i \cdot d\mathbf{J}_k. \quad (7)$$

The n th of the mass fractions and mass fluxes were eliminated, so the last term of Eq. (7) deals with the energy flux as its formal n th component; the concentration term is collected with the differences of the chemical potentials $\mu_n - \mu_i$. [See the end of Sec. I and Eqs. (9)–(11).] This is a simplest possible generalization of the classical Gibbs equation which in the quasilinear case can be written in the concise matrix form

$$s(\mathbf{z}, \mathbf{J}) = s^{eq}(\mathbf{z}) - \frac{1}{2\rho} \mathbf{J} \cdot \mathbf{\Gamma}(\mathbf{z}) \cdot \mathbf{J}, \quad (8)$$

where $\mathbf{\Gamma}$ is the kinetic matrix of the inertial coefficients γ_{ik} . We use the popular notation of de Groot and Mazur [39] for the vector set. We designate

$$\mathbf{z} = \text{col}(y_1, y_2, \dots, y_{n-1}, h) \quad (\text{state matrix}), \quad (9)$$

$$\mathbf{J} = \text{col}(\mathbf{J}_1, \mathbf{J}_2, \dots, \mathbf{J}_{n-1}, \mathbf{J}_q) \quad (\text{flux matrix}), \quad (10)$$

$$\mathbf{u} = \text{col} \left[\frac{\mu_n - \mu_1}{T}, \frac{\mu_n - \mu_2}{T}, \dots, \frac{\mu_n - \mu_{n-1}}{T}, \frac{1}{T} \right] \quad (\text{transfer potential matrix}), \quad (11)$$

$$\mathbf{C} = \left[\frac{\partial \mathbf{z}}{\partial \mathbf{u}} \right]_{\mathbf{J}=0} = \left[\frac{\partial^2 s^{eq}}{\partial z_i \partial z_j} \right]^{-1} \leq 0 \quad (\text{entropy capacity matrix}), \quad (12a)$$

$$\rho^{-1} \mathbf{\Gamma} = [\gamma_{ik}] \equiv - \frac{\partial^2 s}{\partial J_i \partial J_k} \geq 0 \quad (\text{inertial (kinetic) matrix}). \quad (12b)$$

Under our assumptions of constant \mathbf{v} , ρ , and P , the specific enthalpy h is the relevant state variable. Matrix \mathbf{C} has purposely been defined at the static limit ($\mathbf{J}=0$) to make the equilibrium data of direct use. However, this leads to the complications of the Hessian matrix \mathcal{K} of the entropy density ρs corresponding to Eq. (8), and allows one to identify $(\rho \mathbf{C})^{-1}$ with the submatrix of this Hessian only in the close-to-equilibrium approximation,

$$\mathcal{K} = \frac{\partial^2 \rho s}{\partial a_i \partial a_k} = \begin{bmatrix} (\rho \mathbf{C})^{-1} - \frac{1}{2} \mathbf{\Gamma}_{zz} : \mathbf{J} \mathbf{J} & -\mathbf{\Gamma}_z(\mathbf{z}) \mathbf{J} \\ -\mathbf{\Gamma}_z(\mathbf{z}) \mathbf{J} & -\mathbf{\Gamma}(\mathbf{z}) \end{bmatrix} \xrightarrow{\mathbf{J} \rightarrow 0} \begin{bmatrix} (\rho \mathbf{C})^{-1} & 0 \\ 0 & -\mathbf{\Gamma}(\mathbf{z}) \end{bmatrix} \quad (13)$$

where $\mathbf{a} = (\mathbf{z}^T, \mathbf{J}^T)^T$. Amongst the quantities specified above only the evaluation of the inertial matrix $\mathbf{\Gamma}$ might cause some problem. A suitable way leading to $\mathbf{\Gamma}$ is outlined at the end of this section.

As in local equilibrium theory, one may ask about the form of the entropy source which corresponds to the Gibbs equation (7) or with its integrated counterpart Eq. (8). The answer is found by analogy with classical nonequilibrium thermodynamics, by combining the Gibbs equation with the equations describing the conservation laws for mass and energy. Under our assumptions of negligible compressibility and absence of viscosity terms the conservation equations are

$$\rho \frac{dy_i}{dt} = -\mathbf{\nabla} \cdot \mathbf{J}_i, \quad (14)$$

$$\rho \frac{dh}{dt} = -\mathbf{\nabla} \cdot \mathbf{J}_q. \quad (15)$$

From Eqs. (7), (14), and (15) the following entropy balance is obtained:

$$\rho \frac{ds}{dt} = -T^{-1} \mathbf{\nabla} \cdot \mathbf{J}_q - \sum_1^{n-1} \left[\frac{\mu_n - \mu_k}{T} \right] \mathbf{\nabla} \cdot \mathbf{J}_k - \mathbf{J} \cdot \mathbf{\Gamma} \cdot \frac{d\mathbf{J}}{dt}. \quad (16)$$

This can be split into the sum of divergence and source terms,

$$\rho \frac{ds}{dt} = -\mathbf{\nabla} \cdot \left[T^{-1} \left[\mathbf{J}_q - \sum_1^n \mu_k \mathbf{J}_k \right] \right] + \mathbf{J}_q \cdot \mathbf{\nabla} T^{-1} + \sum_1^{n-1} \mathbf{J}_k \cdot \mathbf{\nabla} \left[\frac{\mu_n - \mu_k}{T} \right] - \mathbf{J} \cdot \mathbf{\Gamma} \cdot \frac{d\mathbf{J}}{dt}, \quad (17)$$

where the condition of vanishing sum of all mass fluxes has been used to present the entropy flux in its conventional form, Eq. (19). More concisely (in matrix notation),

$$\rho \frac{ds}{dt} = -\mathbf{\nabla} \cdot \mathbf{J}_s + \mathbf{J} \cdot \left[\mathbf{\nabla} \mathbf{u} - \mathbf{\Gamma} \cdot \frac{d\mathbf{J}}{dt} \right]. \quad (18)$$

Here the diffusive entropy flux \mathbf{J}_s has been defined as

$$\mathbf{J}_s \equiv \mathbf{J} \cdot \mathbf{u} = T^{-1} \left[\mathbf{J}_q - \sum_1^n \mu_k \mathbf{J}_k \right]. \quad (19)$$

The condition of nonnegativeness of the entropy source in Eq. (18) leads to the following matrix phenomenological equation:

$$\mathbf{J} = \mathbf{L} \cdot \left[\nabla \mathbf{u} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right], \quad (20)$$

which simplifies to the well-known classical relationship

$$\mathbf{J} = \mathbf{L} \cdot \nabla \mathbf{u}, \quad (21)$$

when Γ vanishes or G and C_0 tend to infinity. The result obtained, Eq. (20), can be written in the form of the equations

$$\mathbf{J} + \tau \cdot \frac{d\mathbf{J}}{dt} = \mathbf{L} \cdot \nabla \mathbf{u}, \quad (22)$$

$$\tau = \mathbf{L} \cdot \Gamma, \quad (23)$$

which constitute the phenomenological equation and the definition of the relaxation time matrix, respectively. Equation (22) constitutes the matrix generalization of the Maxwell-Cattaneo equation (1). It is remarkable that the moment equations derived from the linearized Boltzmann equation [2,15,65–68] are just in the form of Eq. (22). This equation describes coupled heat and mass diffusion with finite wave speed which, with Eq. (23), define the elements of the relaxation matrix. One may see that the matrix τ has been expressed in terms of the two basic thermodynamic matrices, the inertial matrix Γ (the kinetic entropy Hessian in the flux frame), and the Onsager matrix \mathbf{L} , Eq. (21). The latter is frequently available from experiment. However, the formula (23) is likely to serve to evaluate Γ rather than τ because τ is available, in many cases, in terms of standard quantities. These are the general diffusivity matrix \mathbf{D} and the shear modulus G . They appear in the matrix counterpart of Eq. (5),

$$\tau = -\mathbf{D}/c_0^2 = -\mathbf{D}\rho/G. \quad (24)$$

In the general case including thermal diffusion terms, the matrix of diffusion is related to the Onsager matrix \mathbf{L} by the well-known relation

$$\mathbf{D} = -\rho^{-1} \mathbf{L} \cdot \mathbf{C}^{-1} \quad (25)$$

[39]. Hence Eq. (24) can be written in the simple alternative form

$$\tau = -\mathbf{L} \cdot \mathbf{C}^{-1} / (\rho c_0^2) = -\mathbf{L} \cdot \mathbf{C}^{-1} / G. \quad (26)$$

From Eq. (23), $\Gamma = \mathbf{L}^{-1} \cdot \tau$ and hence the general inertial matrix, in terms of the available quantities, is

$$\Gamma = -\mathbf{C}^{-1} / (\rho c_0^2) = -\mathbf{C}^{-1} / G. \quad (27)$$

For the ideal gas $G = P = \rho RT/M$ and $c_0 = (RT/M)^{1/2}$. When pure heat transfer occurs without mass diffusion, $\mathbf{C} = C = c_\rho T^2 = 5T^2 R / 2M$, which yields $\Gamma_h = -2M / (5RT^2 P) = -2\rho / 5TP^2$, in complete agreement with the kinetic theory, Enskog method [2,14]. The corresponding coefficient in the (specific) energy representation, is that of the square of the entropy flux rather than of the square of heat flux; it equals $\Gamma_e = T^3 C^{-1} / \rho G = T c_\rho^{-1} / \rho G$. (This is because $\Delta e = -T\Delta s$ and $\mathbf{q} = T\mathbf{J}_s$.)

The knowledge of Γ_e allows one to find the general expression for the coefficient g in the nonequilibrium energy surplus $\Delta e = (\frac{1}{2})\rho^{-2}g\mathbf{J}_s^2$, used previously to evaluate the contribution of \mathbf{J}_s to the related Lagrangian [16]. The general formula is $g = T\rho / (c_\rho G)$ yielding for the ideal gas $g = 2m^2 / 5k^2$ in agreement with kinetic theory. The coefficient g also leads to the appropriate value of the thermal conductivity $\lambda = 5RP\tau / 2M$, consistent with the relaxation-time approximation of the Boltzmann equation [16]. When momentum transfer is included the related entry in the matrix \mathbf{C} is $(2T)^{-1}$, yielding $\Gamma_m = -1 / (2PT)$, also in agreement with kinetic theory [2,14].

Finally [69], for the isothermal self-diffusion of the two isotopes A and B where $C_d^{-1} = -RM^{-1}(y_A^{-1} + y_B^{-1})$, the kinetic coefficient $\Gamma_d = -P^{-1}RM^{-1}(y_A^{-1} + y_B^{-1})$. This coefficient preserves the form of the kinetic entropy as the negative ratio of the kinetic energy of diffusion and the absolute temperature. That particular form is in agreement with the Maxwell-Guya law linking the loss of the availability with the change of the entropy.

Thus Eq. (27) generalizes the previous partial findings, including the pure heat transfer [10,43,51,53]. In spite of the above number of results showing the consistency of the formula (27), its physical meaning is intriguing; it does not allow a simple interpretation. This is due to the presence of the static quantities (\mathbf{C} and T , etc.) in the formula for the kinetic quantity Γ . Therefore it should be stressed that the formula only *expresses* the kinetic matrix in terms of the suitable static arguments, but the appropriate interpretation for Γ is the kinetic part of the Hessian of the entropy (per unit volume) $\partial^2 \rho s / \partial \mathbf{J} \partial \mathbf{J}$.

In the front of a one-dimensional thermal wave, the flux contribution to the second derivative of the entropy, under the constant density assumption

$$d^2 \rho s = \frac{1}{2} \frac{\partial^2 \rho s}{\partial \mathbf{J} \partial \mathbf{J}} : \mathbf{J} \mathbf{J} \equiv -\frac{1}{2} \Gamma : \mathbf{J} \mathbf{J} \quad (28)$$

can be expressed in terms of the jump of the state \mathbf{z} throughout the thermal wave front by using the front balance equations. They are quite elementary [55] and yield $\mathbf{J} = \rho c_0 (\mathbf{z} - \mathbf{z}_0)$. Here the subscript zero refers to the undisturbed region; the changes of the density and kinetic energy have been assumed negligible. Substituting this result and Eq. (27) into Eq. (28) yields, under the condition of constant ρ and the close-to-equilibrium approximation Eq. (13),

$$\begin{aligned}
 d^2(\rho s)^{\text{kin}} &= -\frac{1}{2}\Gamma:\mathbf{J}\mathbf{J} = \frac{1}{2}\rho G\Gamma:(\mathbf{z}-\mathbf{z}_0)(\mathbf{z}-\mathbf{z}_0) \\
 &= \frac{1}{2}\rho\mathbf{C}^{-1}:(\mathbf{z}-\mathbf{z}_0)(\mathbf{z}-\mathbf{z}_0) \\
 &= d^2(\rho s)^{\text{stat}}. \tag{29}
 \end{aligned}$$

Hence one can give an interpretation of the formula (27) for this example: it can be regarded as the consequence of the fact that, in the thermal wave front, the kinetic and static contributions to the second differential of the entropy are equal. This is the situation similar to the one in the theory of the infinite lines of the electromagnetic field, for which, in the case of small energy dissipation, the proportionality of inductance to the reciprocal of the capacitance can be assumed, as in our Eq. (27). The electromagnetic result is the consequence of the fact that the electromagnetic field carries equal amounts of magnetic and electric energy [70,71]. The formula (27) can also be an approximation of this sort for not-too-large entropy dissipation and the constant fluid density. The latter assumption could perhaps be relaxed in more general models; however the former seems inevitable. Therefore, while the formula (27) is very useful, we stress that the general results of the next section need not rely on this formula, or on the approximations that lead to Eq. (29). The general results of the following section pertain to expressions containing the kinetic matrix Γ explicitly.

IV. ERROR FUNCTIONAL AND THE VARIATIONAL PRINCIPLE

We will now construct our variational principle describing the coupled wave heat and mass transfer in a multicomponent system. We use Eq. (20) in its original form as well as in the form obtained from evaluation of the inertial matrix of Eq. (27) and close-to-equilibrium

approximation of gradient \mathbf{u} ,

$$\mathbf{J} = \mathbf{L} \cdot \left[\mathbf{C}^{-1}\nabla\mathbf{z} + (G\mathbf{C})^{-1} \cdot \frac{d\mathbf{J}}{dt} \right]. \tag{30}$$

Consider the following error functional, letting $\mathbf{R} = \mathbf{L}^{-1}$:

$$\min \int_{t_1}^{t_2} \frac{1}{2}\mathbf{R}(\mathbf{z}):\mathbf{w}\mathbf{w} dV dt. \tag{31}$$

Here \mathbf{w} is the flux deviation

$$\mathbf{w} = \mathbf{J} - \mathbf{L} \cdot \mathbf{X} \tag{32}$$

between the actual value of the flux \mathbf{J} and its value $\mathbf{L} \cdot \mathbf{X}$ resulting from the action of the generalized force \mathbf{X} . In our model

$$\mathbf{X} = \nabla\mathbf{u} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \approx \mathbf{C}^{-1} \cdot \nabla\mathbf{z} + (G\mathbf{C})^{-1} \cdot \frac{d\mathbf{J}}{dt}, \tag{33}$$

corresponding, respectively, to Eqs. (20) and (30). The last expression shows the thermodynamic force of the linear theory (the case of constant equilibrium values of \mathbf{C} and G). The extension from this linear theory to a "quasilinear form" with a state dependent \mathbf{R} , \mathbf{C} , and Γ and a more exact representation of gradient \mathbf{u} in terms of \mathbf{z} and \mathbf{J} does not change the resulting equation (35) below. However, the working form of the thermodynamic forces [middle term of Eq. (33) in terms of \mathbf{z} and \mathbf{J} , Appendix] becomes more complicated. (In particular, these forces may contain extra space derivative terms contributing to the state dependent Γ .) To avoid lengthy expressions our examples in the main text (Sec. V) are restricted to the linear theory.

When the phenomenological Eq. (20) is satisfied, $\mathbf{w} = \mathbf{0}$. Hence the unique absolute minimum of the functional (31) is zero. In view of the Onsagerian symmetry this gives rise to the equation

$$\begin{aligned}
 \min \int_{t_1}^{t_2} \frac{1}{2}\mathbf{R}(\mathbf{z}):\mathbf{w}\mathbf{w} dV dt &= \min \int_{t_1}^{t_2} \left[\frac{1}{2}\mathbf{R}^{-1}(\mathbf{z}):\mathbf{X}\mathbf{X} + \frac{1}{2}\mathbf{R}(\mathbf{z}):\mathbf{J}\mathbf{J} - \mathbf{X} \cdot \mathbf{J} \right] dV dt \\
 &= \min \int_{t_1}^{t_2} \left[\frac{1}{2}\mathbf{R}^{-1}:\mathbf{X}\mathbf{X} + \frac{1}{2}\mathbf{R}:\mathbf{J}\mathbf{J} - \left(\frac{\partial\rho s}{\partial t} + \nabla \cdot (\mathbf{J}_2 + \rho s\mathbf{v}) \right) \right. \\
 &\quad \left. + \lambda \cdot \left(\frac{\partial\rho\mathbf{z}}{\partial t} + \nabla \cdot (\mathbf{J} + \rho\mathbf{z}\mathbf{v}) \right) \right] dV dt = 0, \tag{34}
 \end{aligned}$$

where \mathbf{J}_s is defined as $\mathbf{J} \cdot \mathbf{u}$ and \mathbf{X} is defined by Eq. (33). Equation (18) has been used to transform the product $\mathbf{X} \cdot \mathbf{J}$ into the four-divergence of the nonequilibrium entropy. But when doing this the very essential point should be remembered that this four-divergence is equivalent to $\mathbf{X} \cdot \mathbf{J}$ only if all the conservation laws are met. Therefore the second line of Eq. (34) contains not only the entropy four-divergence but also the product of a Lagrangian multiplier vector λ and the four-divergence of the balance equations. Only then are the upper and lower line of Eq. (34) equivalent, not only in the sense of their numerical values but also in the sense of their extremum

properties. By overlooking this point, some researchers worked correctly only with the local expression of Eq. (34), the integrand of its upper line (see the discussion in Sec. VI). The presence of both the space and time derivatives in Eq. (34) proves that the integral variational principle must involve the four-dimensional integral over the space and time, even in the limiting parabolic case. Onsager reciprocity and integrability constraints are yet other (algebraic) constraints that should be satisfied. They are obeyed identically by taking \mathbf{L} , \mathbf{C} , and Γ symmetric.

Considering the two four-divergence terms of Eq. (34) we note that the Lagrangian multiplier vector λ must

converge to the transport potential vector \mathbf{u} on the extremal surfaces. This is because only then do the related partial time derivatives compensate in the limiting case of the classical Gibbs equation and the flux terms yield the classical bilinear expression $\mathbf{J} \cdot \text{gradu}$. The entropy four-

divergence can easily be taken out of the integral by using Gauss's theorem. This yields the variational principle describing the second law between the two fixed times t_1 and a subsequent t_2 ,

$$S(t_2) = S(t_1) + \min \left\langle \int_{t_1}^{t_2} -\mathbf{J}_s^{\text{total}} \cdot d\mathbf{A} dt + \int_{t_1}^{t_2} \left[\frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \mathbf{X}\mathbf{X} + \frac{1}{2} \mathbf{R}(\mathbf{z}) : \mathbf{J}\mathbf{J} + \lambda \cdot \left(\frac{\partial \rho \mathbf{z}}{\partial t} + \nabla \cdot (\mathbf{J} + \rho \mathbf{z}\mathbf{v}) \right) \right] dV dt \right\rangle, \quad (35)$$

or briefly $S(t_2) = S(t_1) + \min(S^{\text{diss}} - S^{\text{exch}}$). Here $\mathbf{J}_s^{\text{tot}} = \mathbf{J}_s + \rho \mathbf{s}\mathbf{v}$, and S^{diss} and S^{exch} are the production and exchange components of the entropy functional. The change of the entropy itself is then obtained on the extremal surfaces of the functional $(S^{\text{diss}} - S^{\text{exch}})$, Eq. (35), in course of its minimization. S appears as the state function, in accordance with Bellman's principle of optimality [72].

In order for the functional $(S^{\text{diss}} - S^{\text{exch}})$ to have a minimum one must require that the first variation $\delta(S^{\text{diss}} - S^{\text{exch}}) = 0$, for all admissible $\delta \mathbf{z}$, $\delta \mathbf{J}$, and $\delta \lambda$; in particular that $\delta(S^{\text{diss}} - S^{\text{exch}}) = 0$ for those admissible $\delta \mathbf{z}$, $\delta \mathbf{J}$, and $\delta \lambda$ which vanish on the system boundary. Therefore the Euler-Lagrange equations should always hold for arbitrary (preassigned or free) variations of the generalized state $(\mathbf{J}, \mathbf{z}, \lambda)$ and for any arbitrary (fixed or variable) region of the space-time. Furthermore, the four-dimensional space-time integral of the entropy generation is the only quantity needed to obtain the partial-differential equations governing the process under arbitrary boundary conditions (the main task of this work). However, for the purpose of solving any particular problem, e.g., via direct variational methods, the boundary conditions should be specified. Then, the variation of the surface functional of Eq. (35) serves as the basis for these boundary conditions. For our model this leads to the phenomenological equation (20) or (30) in the form of the natural transversality condition describing vanishing of the normal component of the vector $\mathbf{J} - \mathbf{L} \cdot \mathbf{X}$ on the boundary surface A .

Consequently, to determine the internal behavior of the system in terms of its partial-differential equations, the

minimum should be sought for the four-dimensional (space-time) functional of the entropy production

$$S^{\text{diss}} = \min \int_{t_1}^{t_2} \left[\frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \mathbf{X} \left[\nabla \mathbf{z}, \frac{\partial \mathbf{J}}{\partial t}, \frac{\partial \mathbf{J}}{\partial \mathbf{x}} \right] \times \mathbf{X} \left[\nabla \mathbf{z}, \frac{\partial \mathbf{J}}{\partial t}, \frac{\partial \mathbf{J}}{\partial \mathbf{x}} \right] + \frac{1}{2} \mathbf{R}(\mathbf{z}) : \mathbf{J}\mathbf{J} + \lambda \cdot \left(\frac{\partial \rho \mathbf{z}}{\partial t} + \nabla \cdot (\mathbf{J} + \rho \mathbf{z}\mathbf{v}) \right) \right] dV dt, \quad (36)$$

where the role of the derivatives of the extended state (\mathbf{z}, \mathbf{J}) with respect to the space-time variables (\mathbf{x}, t) has been emphasized. The integrand over the four-volume, or the thermodynamic Lagrangian, is numerically equal to the entropy from the source. However, as seen from Eq. (36), the production from this entropy source has to be expressed in terms of the field variables in a specific way; the *form* of the integrand is essential. To preserve the generality of the formulation, allowing arbitrary (unsteady or steady) behavior with no restriction to frozen fields or a finite wave speed, the two dissipation functions have to be used and the conservation laws must be incorporated. The first dissipation function is the flux dependent

$$\Phi(\mathbf{z}, \mathbf{J}) = \frac{1}{2} \mathbf{R}(\mathbf{z}) : \mathbf{J}\mathbf{J}, \quad (37)$$

and the second is force dependent. Through the forces \mathbf{X} the function Ψ involves the derivatives of the extended state (\mathbf{z}, \mathbf{J}) with respect to the space-time variables (\mathbf{x}, t) ,

$$\begin{aligned} \Psi \left[\mathbf{z}, \nabla \mathbf{z}, \frac{\partial \mathbf{J}}{\partial t}, \frac{\partial \mathbf{J}}{\partial \mathbf{x}} \right] &= \frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \mathbf{X}\mathbf{X} \\ &= \frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \left[\nabla \mathbf{u} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \left[\nabla \mathbf{u} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \\ &= \frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \left[\left[\mathbf{C}^{-1} - \frac{\Gamma_{zz}}{2\rho} \right] \cdot \nabla \mathbf{z} - \frac{\Gamma_z}{\rho} (\mathbf{J} \cdot \nabla) \mathbf{J} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \left[\left[\mathbf{C}^{-1} - \frac{\Gamma_{zz}}{2\rho} \right] \cdot \nabla \mathbf{z} - \frac{\Gamma_z}{\rho} (\mathbf{J} \cdot \nabla) \mathbf{J} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right]. \end{aligned} \quad (38)$$

In the last line of this equation, Eqs. (8) and (13) were used to express the gradient of \mathbf{u} in terms of gradients of \mathbf{z} and \mathbf{J} . In the linear theory the terms with Γ_z and Γ_{zz} are ignored and matrices \mathbf{C} and Γ are evaluated at equilibrium. It is easy to see that the numerical values of

both dissipation functions are equal, i.e., $\Phi = \Psi$, when the phenomenological equation holds (Onsagerian property).

The working form of the functional describing the linear coupled-wave transfer of the energy and mass is

$$S^{\text{diss}} = \min \int_{t_1}^{t_2} \left[\frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \left[\mathbf{C}^{-1} \cdot \nabla \mathbf{z} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \left[\mathbf{C}^{-1} \cdot \nabla \mathbf{z} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] + \frac{1}{2} \mathbf{R}(\mathbf{z}) : \mathbf{J} \mathbf{J} + \lambda \cdot \left[\frac{\partial \rho \mathbf{z}}{\partial t} + \nabla \cdot (\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \right] \right] dV dt, \quad (39)$$

where the evaluation of (27) of the matrix Γ as $-\mathbf{C}^{-1}/G$ can be used. The more complicated counterpart in “quasilinear theory” is obvious in view of the third line of Eq. (38); generalizations of this sort need not, in principle, be written down here; see, however, Eq. (41) and the Appendix. To determine the governing partial-differential equations we extremize the dissipation integral with respect to the field variables \mathbf{z} , \mathbf{J} , and λ , or $\rho \mathbf{z}$, \mathbf{J} , and λ . (The mass density ρ is the constant parameter only since the convection is uniform.)

It is known from variational calculus that the integrands of functionals can be “gauged” by adding (or subtracting) to them any four-divergence term since it does not change the equations of motion. Gauge transformations occasionally lead to more manageable forms

than the original integrand; from gauged forms, for example, certain integrals can more easily be separated. An equivalent, manageable form of the functional (39) is obtained by transforming its λ term into the following sum:

$$\Sigma = \frac{\partial(\rho \mathbf{z} \cdot \lambda)}{\partial t} + \nabla \cdot [(\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \cdot \lambda] - \rho \mathbf{z} \cdot \frac{\partial \lambda}{\partial t} - (\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \cdot \nabla \lambda. \quad (40)$$

The four-divergence is rejected and the functional (39) takes the form containing λ through its derivatives only. However, we give a generalization of this result corresponding to the “quasilinear theory,” where all the terms in the last line of Eq. (38) are essential,

$$-S^{T\text{diss}} = \min \int_{t_1}^{t_2} \left\{ \frac{1}{2} \mathbf{R}^{-1}(\mathbf{z}) : \left[\left[\mathbf{C}^{-1} - \frac{\Gamma_{zz}}{2\rho} \right] \cdot \nabla \mathbf{z} - \frac{\Gamma_z}{\rho} (\mathbf{J} \cdot \nabla) \mathbf{J} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \left[\left[\mathbf{C}^{-1} - \frac{\Gamma_{zz}}{2\rho} \right] \cdot \nabla \mathbf{z} - \frac{\Gamma_z}{\rho} (\mathbf{J} \cdot \nabla) \mathbf{J} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] + \frac{1}{2} \mathbf{R}(\mathbf{z}) : \mathbf{J} \mathbf{J} - \rho \mathbf{z} \cdot \frac{\partial \lambda}{\partial t} - (\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \cdot \nabla \lambda \right\} dV dt \quad (41)$$

(see the transfer equations corresponding to this “quasilinear theory” in the Appendix). The superscript T pertains to the transformed version of the original S^{diss} (see explanation of the negative sign below). The form (41) has some advantage when the nonequilibrium reciprocal temperature and Planck potentials are the state variables since they are represented by the components of λ . In the linear theory the evaluation (27) of the matrix Γ as $-\mathbf{C}^{-1}/G$ can be used at equilibrium, and the terms with derivatives of Γ ignored.

Then

$$-S^{T\text{diss}} = \min \int_{t_1}^{t_2} \left[\frac{1}{2} \mathbf{W}(\mathbf{z}) : \left[\nabla \mathbf{z} + \frac{d\mathbf{J}}{G dt} \right] \left[\nabla \mathbf{z} + \frac{d\mathbf{J}}{G dt} \right] + \frac{1}{2} \mathbf{R}(\mathbf{u}) : \mathbf{J} \mathbf{J} - \rho \mathbf{z} \cdot \frac{\partial \lambda}{\partial t} - (\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \cdot \nabla \lambda \right] dV dt, \quad (42)$$

where \mathbf{W} is the new symmetric matrix defined as

$$\mathbf{W} = (\mathbf{C}^{-1})^T \cdot \mathbf{R}^{-1} \cdot \mathbf{C}^{-1} = (\mathbf{C} \cdot \mathbf{R} \cdot \mathbf{C})^{-1}. \quad (43)$$

The integrand of the functional (41) or (42) is no longer equal to the entropy production. Its physical interpretation is the complete negative thermodynamic Legendre transformation of entropy at disequilibrium, $-s^T(\mathbf{u}, \mathbf{w})$, where $\mathbf{w} = -\Gamma \cdot \mathbf{J}$ is the thermodynamic conjugate of \mathbf{J} . This corresponds to the Mathieu function $-P/T$ at equilibrium. In this regard it is worth pointing out the role of the Legendre transform of the entropy in fluctuation theory [73].

The conservation laws can be satisfied identically after introducing the so-called Biot vector [74],

$$\mathbf{J} + \rho \mathbf{z} \mathbf{v} = \frac{\partial \mathbf{H}}{\partial t}, \quad (44)$$

with

$$\rho \mathbf{z} = -\nabla \cdot \mathbf{H}. \quad (45)$$

When these representations of \mathbf{J} and \mathbf{z} are substituted into the entropy functional (38) the λ term disappears and the process can be described without any loss in the generality by a functional of the single vector \mathbf{H} . The

price paid for this apparent simplification is that the entropy functional in this case involves the second derivatives of the vector \mathbf{H} with respect to the space and time coordinates. This is not surprising in the case of irreversible processes. The corresponding Euler-Lagrange equation is complex (the second-order variational problem), although the resulting thermodynamic equations of motion (in terms of the \mathbf{J} and \mathbf{z} variables) are the same.

It is also worth pointing out that the squaring procedure in the error expression \mathbf{w} , Eq. (31), had introduced the second solution for the flux \mathbf{J} . Besides Eq. (20), one also has

$$-\mathbf{J} = \mathbf{L} \cdot \left[\nabla \mathbf{u} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right], \quad (46)$$

with the sign of \mathbf{J} reversed. This is the mirror-image solution (for $t' = -t$) corresponding with the growth of the heat fluctuations and the related decrease of the entropy. The so-called antithermodynamic branch is of course enormously less probable than the thermodynamic one.

V. EQUATIONS OF TRANSFER FROM THE ENTROPY FUNCTIONAL

Any variational formulation has virtue of conciseness: the single equation for the scalar quantity (here, the total entropy generated) stands for the whole set of the differential equations. Physical insight is achieved more easily when one follows the properties of the single physical scalar rather than the whole set of related equations. Moreover, with a functional at our disposal, various direct variational methods can be applied to obtain approximate solutions, which exhibit, as a rule, very good accuracy [75].

Here we show a linear equation set resulting from extremizing the functional (42). The Euler-Lagrange equation for the vector λ constitutes the conservation equation,

$$\frac{\partial \rho \mathbf{z}}{\partial t} + \nabla \cdot (\mathbf{J} + \rho \mathbf{z} \mathbf{u}) = 0. \quad (47)$$

This is the matrix form of the conservation laws for mass and energy, Eqs. (14) and (15). The stationary value of the multiplier vector is the nonequilibrium transport potential vector, Eq. (11),

$$\lambda = \mathbf{u}. \quad (48)$$

It is interesting that an analogous interpretation of the Lagrange multipliers appears in information-theoretic thermodynamics although that formulation is different: it pertains to the maximum of the entropy with respect to the initial distribution over the states, and those multipliers are equilibrium quantities [76]. The stationarity condition of the entropy functional (42) with respect to the flux vector \mathbf{J} has the form

$$\mathbf{R} \cdot \mathbf{J} = \nabla \lambda - \frac{d}{dt} \left[\Gamma \cdot \mathbf{R}^{-1} \cdot \left[\mathbf{C}^{-1} \nabla \mathbf{z} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right] \right], \quad (49)$$

with $\Gamma = -\mathbf{C}^{-1}/G$, Eq. (27). On the stationary surfaces

of the functional (42), where $\lambda = \mathbf{u}$, this equation is obeyed by the generalized Fourier-Fick equation (20) and its mirror image, Eq. (46), in the form of the extended Fick equation,

$$\mathbf{J} = -\rho \mathbf{D} \cdot \left[\nabla \mathbf{z} + \frac{d\mathbf{J}}{G dt} \right], \quad (20')$$

$$-\mathbf{J} = -\rho \mathbf{D} \cdot \left[\nabla \mathbf{z} + \frac{d\mathbf{J}}{G dt} \right]. \quad (46')$$

For Γ of Eq. (27) the stationarity condition of the entropy functional with respect to the state vector \mathbf{z} is the matrix wave equation of change,

$$\mathbf{C} \cdot \frac{d\lambda}{dt} = \mathbf{D} \cdot \left[\nabla^2 \mathbf{z} - \frac{d^2 \mathbf{z}}{c_0^2 dt^2} \right], \quad (50)$$

yielding at $\lambda = \mathbf{u}$ the wave equation of diffusion,

$$\frac{d\mathbf{z}}{dt} = \mathbf{D} \cdot \left[\nabla^2 \mathbf{z} - \frac{d^2 \mathbf{z}}{c_0^2 dt^2} \right]. \quad (51)$$

The flux associate of the above equation,

$$\frac{d\mathbf{J}}{dt} = \mathbf{D} \cdot \left[\nabla^2 \mathbf{J} - \frac{d^2 \mathbf{J}}{c_0^2 dt^2} \right], \quad (52)$$

results from combining the stationarity conditions of the entropy functional with respect to the variables \mathbf{J} and λ under the condition of the vanishing vorticity of the flux \mathbf{J} ,

$$\nabla \times \mathbf{J} = \mathbf{0}, \quad (53)$$

obeyed by Eqs. (20) and (49). On the other hand, taking the divergence of the phenomenological equation (20), and using the conservation laws, Eqs. (14) and (15) or Eq. (47), the same matrix wave equation is obtained.

If, instead of the state variables \mathbf{z} , Eq. (9), the transport potentials, Eq. (11), are used, an alternative form is found,

$$\rho \mathbf{C} \cdot \frac{d\mathbf{u}}{dt} = -\mathbf{L} \cdot \left[\nabla^2 \mathbf{u} - \frac{d^2 \mathbf{u}}{c_0^2 dt^2} \right]. \quad (54)$$

The flux associate of Eq. (54),

$$\rho \mathbf{C} \cdot \frac{d\mathbf{I}}{dt} = -\mathbf{L} \cdot \left[\nabla^2 \mathbf{I} - \frac{d^2 \mathbf{I}}{c_0^2 dt^2} \right], \quad (55)$$

is the simple transformation of Eq. (52) with the new vector $\mathbf{I} = (\rho \mathbf{C})^{-1} \mathbf{J}$. It characterizes diffusive transport in terms of intensive rather than extensive quantities; in the linear case the components of \mathbf{I} are products of the transport potentials \mathbf{u} and corresponding velocities of diffusion $\mathbf{v}_i = \mathbf{J}_i / (\rho \mathbf{z}_i)$, $i = 1, 2, \dots, n$. In resting systems the substantial derivatives simplify to the partial derivatives and Eqs. (50)–(52), (54), and (55) contain on their right sides d'Alembertians instead of the usual Laplacians of standard parabolic models.

The above equations hold for arbitrary boundary con-

ditions; the latter can, however, be obtained from the general Eq. (35) too. When the state variables and their derivatives are varied on the boundary surface A , the surface integral of Eq. (35) plays a role. For free variations of the state the transversality condition results in the form of the phenomenological equation (30) describing the vanishing of the normal component of the vector $\mathbf{J} - \mathbf{L} \cdot \mathbf{X}$ on the boundary A ; see [4,65–68] for a thorough physical discussion.

The physical content of Eqs. (51) and (54) is obscured by their matrix form. We operate here with the not-so-common quantities \mathbf{z} and \mathbf{u} . Therefore another representation is useful where the fluxes, forces, and diffusivities are transformed to the quantities related to the sensible heat flux $\mathbf{J}_h = \mathbf{J}_q - \sum_k h_k \mathbf{J}_k$ rather than to the irreversible energy flux \mathbf{J}_q . As a result of such transformations the following wave system is obtained:

$$\frac{d\mathbf{y}}{dt} = \mathbf{D}_m \cdot \left[\nabla^2 \mathbf{y} - \frac{d^2 \mathbf{y}}{c_0^2 dt^2} \right] + \frac{\mathbf{D}_T}{T} \left[\nabla^2 T - \frac{d^2 T}{c_0^2 dt^2} \right], \quad (56)$$

$$\rho C_p \frac{dT}{dt} = -\rho T \mathbf{D}_T^T \mathbf{C}_m^{-1} \cdot \left[\nabla^2 \mathbf{y} - \frac{d^2 \mathbf{y}}{c_0^2 dt^2} \right] + \lambda \left[\nabla^2 T - \frac{d^2 T}{c_0^2 dt^2} \right], \quad (57)$$

with

$$\mathbf{C} = \text{diag}(\mathbf{C}_m^{-1}, -C_p^{-1} T^2), \quad \mathbf{D}_T = (\rho T)^{-1} \mathbf{L}_T. \quad (58)$$

Here \mathbf{L}_T is the part of Onsager's matrix related to the thermal diffusion. This set operates with the most common variables, temperature T and concentrations y_i and simplifies to the classical set [39] for c_0 approaching infinity. It is expected that Eqs. (56) and (57) will describe heat and mass transport better than the classical equations, especially in highly nonstationary cases, e.g., during the travel of sound and especially shock waves, of electromagnetic waves through a medium with thermal diffusion, or of ultrasonic or dielectric drying of solutions of solids—in general, when heat transfer or change of local thermodynamic variables occurs at a rate comparable to the internal relaxation of the system. An illustration is the equation set of the “quasilinear generalization” in the Appendix.

VI. RELATION TO PREVIOUS APPROACHES

Onsager [77] proposed the local quasivariational principle whereby the phenomenological laws are obtained from a prescription of making stationary the restricted variation (frozen \mathbf{u}) of the expression for power:

$$\min \int_v (\frac{1}{2} \mathbf{R} : \mathbf{J} \mathbf{J} - \mathbf{J} \cdot \nabla \mathbf{u}) dV. \quad (59)$$

This yields $\mathbf{J} = \mathbf{L} \cdot \mathbf{X}$ as the only outcome. Approaches related to Eq. (59) were pursued later in many works, e.g., [35,39,78]. The explorations with frozen fields culminated in the method of the local potential [31] but it was at the same time seriously criticized as physically dubious [29,30]. Gyarmati's local principle [35] shifted the problem from the space of \mathbf{J} and \mathbf{u} into the space of \mathbf{J} and \mathbf{X}

which was not really constructive. It was an advance, nevertheless, because it relaxed the frozen force requirement by introducing the trivial (derivativeless) criterion,

$$\min \int_v (\frac{1}{2} \mathbf{R}^{-1} : \mathbf{X} \mathbf{X} + \frac{1}{2} \mathbf{R} : \mathbf{J} \mathbf{J} - \mathbf{X} \cdot \mathbf{J}) dV. \quad (60)$$

Note that there is no integration with respect to the time here. Minimizing this expression with respect to either \mathbf{X} or \mathbf{J} yields the same equation $\mathbf{J} = \mathbf{L} \cdot \mathbf{X}$, since $\mathbf{R}^{-1} = \mathbf{L}$. If the classical representation $\mathbf{X} = \text{gradu}$ is substituted into Eq. (60) then the so-modified functional (with \mathbf{J} and \mathbf{u} the variables) yields $\mathbf{J} = \mathbf{L} \cdot \text{gradu}$ and $\text{div}(\mathbf{J} - \mathbf{L} \cdot \text{gradu}) = 0$, by independent variation of \mathbf{J} and \mathbf{u} , respectively. The latter result is a consequence of the former. While they both are correct the set is incomplete; the conservation laws do not follow from Eq. (60) and hence the related parabolic equations of change cannot be derived unless one applies the artificial restricted variations to a transformed version of Eq. (60).

Onsager's functional (59) can be distinguished from our functional (41) in the steady-state case. Indeed, let us consider the parabolic counterpart of Eq. (41),

$$-S^{T\text{diss}} = \min \int_{t_1}^{t_2} \left[\frac{1}{2} \mathbf{R}^{-1} : (\mathbf{C}^{-1} \cdot \nabla \mathbf{z})(\mathbf{C}^{-1} \cdot \nabla \mathbf{z}) + \frac{1}{2} \mathbf{R} : \mathbf{J} \mathbf{J} - \rho \mathbf{z} \cdot \frac{\partial \lambda}{\partial t} - (\mathbf{J} + \rho \mathbf{z} \mathbf{v}) \cdot \nabla \lambda \right] dV dt. \quad (61)$$

In the steady-state situation the derivatives $\partial \lambda / \partial t$ vanish. Then, when only \mathbf{J} is varied and λ converges to \mathbf{u} on the extremal surfaces, Onsager's equation (60) and hence the Fourier-Onsager structure result from Eqs. (61) or (41) as steady-state conditions. In that sense Onsager's formulation is limited to the steady state. In the nonsteady situation Eq. (61) yields, as the Euler-Lagrange equations with respect to the variables λ , \mathbf{J} , and \mathbf{z} , a more general outcome. It is the parabolic set representing (at $\lambda = \mathbf{u}$) the classical linear model of the unsteady heat and mass transfer,

$$\rho \frac{d\mathbf{z}}{dt} + \nabla \cdot \mathbf{J} = 0, \quad (62)$$

$$\mathbf{R} \cdot \mathbf{J} = \nabla \lambda, \quad (63)$$

$$\rho \mathbf{C} \cdot \frac{d\lambda}{dt} = \rho \mathbf{D} \cdot \nabla^2 \mathbf{z} = -\mathbf{L} \cdot \nabla^2 \mathbf{u}, \quad (64)$$

where Eq. (62) is equivalent to the conservation equation (47). The distinction between $d\lambda$ and $\mathbf{C}^{-1} \cdot d\mathbf{z}$ is implied by the above set. However, the nonequilibrium field λ converges to the field \mathbf{u} , such that $d\mathbf{u} = \mathbf{C}^{-1} \cdot d\mathbf{z}$, as our experience proves. Then the three above equations become dependent, the third resulting from the first two. This is well known from the classical theory. The possibility of independent $d\lambda$ and $d\mathbf{u} = \mathbf{C}^{-1} \cdot d\mathbf{z}$ proves that in the parabolic description (consistent with local equilibrium) it is impossible to preserve the entropy or any other thermodynamic variable in terms of the classical state \mathbf{z} only. The entropy becomes a function of the extended state $(\mathbf{z}, \mathbf{J}, \dots)$, in agreement with Truesdell's equipres-

ence principle and extended thermodynamics [2]. Even more can be said: as our work in progress shows, the entropy and its source can be put into a single canonical formalism yielding a fundamental equation and associated evolution equations. This fundamental equation coincides with the classical one only at equilibrium.

The formulation given in this work is physically acceptable insofar as it shows that any coupled heat and mass transfer process operates so that the increase of the total entropy generated is a minimum, subject also to the constraints defining the process. This principle holds equally well for the hyperbolic theory and the limiting parabolic theory as an exact (i.e., unrestricted type) variational principle provided that the distinction between the fields λ and \mathbf{u} is made for a system away from equilibrium. At the steady state, its parabolic version, Eq. (61), resembles the "governing principle of the dissipative processes" [35]. However, the related integral formulation of Gyarmati for unsteady states suffers the limitation characteristic of the constrained (quasivariational) formulation, namely its time derivative is frozen to be that of the classical state [4,35].

The three-dimensional integral over the volume (used even for the unsteady-state processes) should be contrasted with the four-dimensional space-time integral treated in this work. Working in three space-like dimensions, one must of course freeze the time derivatives; there is no place for them in the three-dimensional Euler-Lagrange equation. However, little has been written so far about the limitations of such formulations. Our embedding of the process in the four-dimensional space-time has resulted in the following benefits: physical insight into the related functionals in terms of the entropy state function rather than entropy production, interpretation of the Lagrangian multipliers as the nonequilibrium thermodynamic intensities, removal of artificial frozen fields, and the nontruncated field equations. Topics of the research in progress include the convergence problems of the variational solutions (related to the stability of equilibrium and nonequilibrium asymptotic states) and the nonlinear generalizations of the variational principle.

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APPENDIX: EQUATIONS OF CHANGE IN QUASILINEAR THEORY

The transport potentials $\partial s/\partial z$, of the quasilinear theory [Eq. (8) with z -dependent Γ], are given by

$$\mathbf{u} = \mathbf{u}^{\text{eq}} - \frac{1}{2\rho} \mathbf{J} \cdot \Gamma_s(z) \cdot \mathbf{J}, \quad (\text{A1})$$

corresponding with the nontruncated dissipation function, Eq. (38), and the entropy functional, Eq. (41). While the phenomenological equation preserves the form (20), new terms appear when it is expressed in terms of the extended state \mathbf{z}, \mathbf{J} ,

$$\mathbf{J} = \mathbf{L}(z) \cdot \left[\left[\mathbf{C}^{-1} - \frac{\Gamma_{zz} : \mathbf{J}\mathbf{J}}{2\rho} \right] \cdot \nabla \mathbf{z} - \frac{\Gamma_z}{\rho} (\mathbf{J} \cdot \nabla) \mathbf{J} - \Gamma \cdot \frac{d\mathbf{J}}{dt} \right]. \quad (\text{A2})$$

The equations of change for \mathbf{z} and \mathbf{J} may again be obtained via minimizing the entropy functional (41). They are now coupled with respect to \mathbf{z} and \mathbf{J} ,

$$\begin{aligned} \frac{d\mathbf{z}}{dt} = & \mathbf{D} \cdot \left[\left[1 - \mathbf{C} \cdot \frac{\Gamma_{zz} : \mathbf{J}\mathbf{J}}{2\rho} \right] \cdot \nabla^2 \mathbf{z} - \frac{d^2 \mathbf{z}}{c_0^2 dt^2} \right] \\ & + \nabla \mathbf{z} \cdot \nabla \left[\mathbf{D} \cdot \left[1 - \mathbf{C} \cdot \frac{\Gamma_{zz}}{2\rho} \right] \right] \\ & - \rho^{-1} \nabla \cdot [\mathbf{D} \cdot \mathbf{C} \cdot \Gamma_z \cdot (\mathbf{J} \cdot \nabla) \mathbf{J}] + \rho^{-1} \frac{d\mathbf{J}}{dt} \cdot \nabla \tau \end{aligned} \quad (\text{A3})$$

and

$$\begin{aligned} \frac{d\mathbf{J}}{dt} = & \mathbf{D} \cdot \left[\left[1 - \mathbf{C} \cdot \frac{\Gamma_{zz} : \mathbf{J}\mathbf{J}}{2\rho} \right] \cdot \nabla^2 \mathbf{J} - \frac{d^2 \mathbf{J}}{c_0^2 dt^2} \right] \\ & - \rho \nabla \mathbf{z} \frac{d}{dt} \left[\mathbf{D} \cdot \left[1 - \mathbf{C} \cdot \frac{\Gamma_{zz}}{2\rho} \right] \right] \\ & + \frac{d}{dt} [\mathbf{D} \cdot \mathbf{C} \cdot \Gamma_z \cdot (\mathbf{J} \cdot \nabla) \mathbf{J}] - \frac{d\mathbf{J}}{dt} \cdot \frac{d\tau}{dt}. \end{aligned} \quad (\text{A4})$$

When the terms with the derivatives of Γ are ignored and the coefficients are constants evaluated at equilibrium (the linear theory), these equations go into the decoupled set, Eqs. (51) and (52). The first of the Eqs. (A3) can also be obtained by taking the divergence of Eq. (A2) and combining it with the conservation law, Eq. (47); the second, (A4) by taking the total time derivative of Eq. (A2) and using this conservation law. In future work we will show that an essential simplification of the equations of this sort can be achieved when a canonical nonlinear formalism is used.

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