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Revised Interpretation of Work Potential in Thermophysical Processes

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An alternative development is attempted of the concept of exergy or availability by introducing the idea that exergy represents an abstract thermodynamic metric that, essentially, quantifies the distance from the state of equilibrium with respect to a given reference value. Traditional and textbook approaches usually develop exergy as a system's potential to do reversible work. Usually, combining the balance of energy and entropy equations makes it possible to construct a corresponding balance of exergy and to use its definition to interpret the resulting terms. In contrast, the essential elements presented deal with the mathematical property of concavity of the entropy as the essence of the second law and how this property translates into a geometric complementarity relation between entropy and exergy. The balance of exergy equation is presented as an expression representing the corresponding convexity of the exergy, again demonstrating a mathematical property intrinsic to the second law.

Nomenclature

E = total energy density
e = total specific energy
g = gravitational acceleration constant
H = enthalpy density
h = specific enthalpy
I = flux or current of quantity
k = coefficient of thermal conductivity
M = molecular mass
m = mass
P = thermodynamic pressure
$\mathcal{Q}$ = thermal energy transfer rate (heating)
R = gas constant
S = entropy density
s = specific entropy
T = temperature
t = time
U = internal energy density
u = specific internal energy
V = volume
$\mathcal{V}$ = fluid velocity
v = specific volume
$\mathcal{W}$ = mechanical energy transfer rate (working)
X = exergy density (also known as availability)
x_k = Cartesian coordinates
z = elevation level in a gravitational field
β = thermal expansion coefficient
γ = ratio of specific heats
Δ = total change in quantity
δ_{ij} = Kronecker delta
κ = isothermal compressibility
λ = second coefficient of viscosity
μ = first coefficient of viscosity
ξ = generic variable
ρ = mass density
τ_{ij} = viscous stress tensor
ϕ = specific exergy
ψ = specific flow exergy

Subscripts

des = destruction or consumption
gen = generation or production
in = transferred into system
out = transferred out of system

Introduction

SCIENTIFIC practice contains certain essential elements of flexibility and adaptability that make progress possible. By incorporating new discoveries, novel perspectives, or fundamental modifications to the conceptual structure of science, the field advances. In the engineering field, the same holds true, especially with the rapid advances made in technology this century. Fluid mechanics, heat transfer, and thermodynamics in particular today exist as mature, yet dynamic fields where progress continues primarily due to the advent of computational modeling and simulation. Of the three, thermodynamics appears still to suffer from an ongoing crisis evident in the continuous reformulation of its foundations.[1] Also, as still currently taught, thermodynamics differs from fluid mechanics and heat transfer where mathematical treatment is possible and easily accessible to most undergraduate engineering students with training in calculus, algebra, and elementary analysis.

Common to fluid mechanics and heat transfer is the concept of the continuum whereby the field variables depend on space and time. Thermodynamics, at least as taught in many universities, does not really make this explicit and often confuses the novice with the introduction of differential operators with ambiguous or nonstandard meaning, for example, δQ, δW, etc. It appears that a more rational approach would alleviate, if not eliminate, this discrepancy that presents thermodynamics in such a different light compared to fluid mechanics and heat transfer. All three fields are intrinsically connected, and it would help in learning each to acknowledge and utilize this connection. Several prominent researchers have carried out much of this important work in the past 30 or 40 years.[1–3] Indicative of the maturity this approach has reached, some recent monographs and books have already appeared that provide a unified treatment.[4–6] The modest contribution that the present work makes consists in the revision of the interpretation usually given to the concept of exergy or availability. Specifically, this will demonstrate that, given the essence of the second law of thermodynamics as a statement of existence for entropy, with particular mathematical properties, a corresponding statement for existence of exergy follows. Subsequently, one may prove that the exergy represents an abstract, mathematical distance functional. Hence, one may correctly interpret the concept of exergy as a thermodynamic functional representing the

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distance of a given system from the state of equilibrium at a reference state.

The author is well aware of the engineering advances made using classical thermodynamics and the concept of exergy as work potential or maximum useful work.[7–9] Common to all of these analyses, however, is the identification of exergy with some kind of work. For example, Ref. 10 notes various attempts to define exergy as "the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium. . . ." Similar definitions may be found in Ref. 11, page 114, and Ref. 12, pages 31 and 32. Although engineers have accepted the capacity to do work as a measure of quality of energy, this does not invalidate another, less anthropomorphic approach. By conceptualizing exergy as a distance functional one eliminates the need to introduce additional terms also found in the literature (e.g., anergy, essergy, etc.) or to fragment exergy into multiple forms as is done with energy. The literature on the subject of availability analysis is quite large and sometimes original sources difficult to find. The interested reader can find a concise and critical review of the origins and history in Refs. 10–14.

Organization of the paper follows this outline: First, certain elements common to classical mechanics are identified broadly. Second, basic thermodynamic theory is presented in a modified way to emphasize the connection to classical mechanics, without introducing nonstandard mathematical notation or ambigous notions about quasi- processes. Third, the mathematical property of entropy is identified and shown to represent the essence of the second law of thermodynamics. Fourth, the concept of exergy is introduced and developed in a way typical of the standard approach but with notation consistent with the rest of the paper. Fifth, the balance of exergy for control mass and control volume are derived, also in the typical way. Sixth, a revised approach is presented that highlights the concavity property of entropy and demonstrates the corresponding convexity of exergy as a function of the independent thermodynamic variables. Last, the idea of exergy as an abstract metric is shown to have merit using the mathematical definition for a distance functional. The extension to continuum thermomechanics is also noted.

Common Elements of Mechanics

The primitive elements of mechanics include bodies, motions, and forces.[15] Certain assumptions or natural laws govern these elements that describe mechanics as a whole. The laws of mechanics abstract the features common to all mechanical phenomena. In a complementary sense, the introduction of constitutive relations illustrates the general principles and provides an abstraction of the differences among material bodies. Essentially, constitutive equations model the response of different kinds of bodies to mechanical stimulus. By defining ideal materials, constitutive relations represent limited aspects of the different material bodies subject to the natural laws in a physical representation of the world. In fluid mechanics, the governing equations are based on the physical principles stipulating the conservation of mass and energy and the balance of momentum, generalized from Newton's second law. In contrast to the mathematical development of fluid mechanics is that usually taken with thermodynamics, in which standard presentations spend much time connecting the principles, terminology, and concepts to real-world examples. This attempt to link the science to the real world often fails to clarify thermodynamics. Usually, it serves only to confound the difference between mathematical equations that express general physical principles and the constitutive relations that allow us to model the particular behavior of material bodies.

Thermodynamics

Thermodynamics began as the science of heat, intended to provide an extended mechanics that would account for a very common experience, namely, that doing work on a body sometimes makes it hotter and sometimes heating a body causes it to do work.[15] Developing thermodynamics in conformity with the common elements of mechanics requires only that we continue to make it clear that the variables are functions of time and space. In general, because common experience tells us that mechanical action does not always result in a mechanical response, we need to add the concept of heating alongside the concept of working or power. Thermodynamics, therefore, requires the statement of the general principles or laws governing all thermodynamic processes and the addition of constitutive relations that model the particular response of a special class of materials. Material bodies with no local deformation or variations in temperature constitute the intended application of elementary thermodynamics. Such a theory, therefore, applies to homogeneous processes where all quantities depend only on time.

For a simple homogeneous substance, the primitive variables include time t, the independent variable, temperature T, volume V, internal energy U, working or work rate $\mathcal{W}$, and heating $\mathcal{Q}$. Abstracting again from common experience, pioneers in the science of thermal mechanics hit on the concept of entropy, which represents that an upper bound to the heating exists. This paper represents that principle in its most general form, namely, by stating an axiom for the existence of entropy and the essence of the second law as representing a particular mathematical property of the entropy with respect to the other thermodynamic variables.

In mechanics, the concept of place and motion at a given time was the focus of analysis. In thermodynamics, the concept of state and process focus on the temperature and other variables at a given time. The state of a material body denoting our system is a set of $k + 1$ functions of time,

$$T(t), \Xi_1(t), \Xi_2(t), \ldots, \Xi_k(t) \tag{1}$$

where the k parameters represent quantities given a priori. The general theory requires no specific interpretation, but for simplicity we will reduce the set to only the volume $V(t)$. Also, at any one time T, V, $\dot{T}$, and $\dot{V}$ may assume any real values subject only to the restriction that $T \geq 0$ on the absolute (Kelvin) scale and $V \geq 0$.

A thermodynamic process is represented by values of the temperature, volume, energy, entropy, working, and heating of the body as functions of time: $T(t)$, $V(t)$, $U(t)$, $S(t)$, $\mathcal{W}(t)$, and $\mathcal{Q}(t)$. These must satisfy the general axioms of thermodynamics. Of course, other variables often desired include the pressure, enthalpy, and Helmholtz free energy. Consider for illustration the temperature and volume as the thermodynamically independent variables, in the sense that $U = U(T, V)$ corresponds to a constitutive relation to be determined. The definition of equilibrium requires that $T(t)$, $V(t) =$ const. The general axioms or first and second laws deal with the concepts of energy and entropy. The first law, in its most abstract form stipulates simply the existence of a thermodynamic property called energy. Mathematically, we have, where $\exists U \ni$,

$$\mathcal{Q} + \mathcal{W} = \dot{U} \tag{2}$$

where $\dot{U}$ represents the time rate of change in the internal energy U. Classical equations of state postulate that the working is purely mechanical and linear in the time rate of change of the volume:

$$\mathcal{W} = -P(T, V)\dot{V} \tag{3}$$

Solving Eq. (2) for the heating and using the chain rule for the differential change in energy due to a differential change in temperature gives

$$\mathcal{Q} = C_V\dot{T} + P\dot{V} \tag{4}$$

where $C_V \equiv \partial U/\partial T$ defines the temperature coefficient of energy.

Second Law

Formulation of the second law for general natural phenomena can be given as a balance of entropy equation given as

$$\dot{S}_{\text{gen}} = \dot{S} + I_S \tag{5}$$

where $\dot{S}_{\text{gen}}$ represents the rate of entropy generation, $\dot{S}$ the time rate of change of entropy contained by the substance, and I_S the entropy current density due to mass, heating, or both. The second law then stipulates that the rate of entropy generation must be nonnegative in all thermophysical processes:

$$\dot{S}_{\text{gen}} \geq 0 \tag{6}$$

Let us consider a rigid material body at some temperature T immersed in a thermal reservoir at temperature T_0, for example, a hot rock inside a cool room. Suppose $T > T_0$ and we let the cooling process proceed from the initial time t to t_0 when the body reaches thermodynamic equilibrium with its surroundings. The transfer of energy as the body cools, from Eq. (2), equals

$$\begin{aligned} \int_t^{t_0} \mathcal{Q}\,\mathrm{d}t &= \int_t^{t_0} \dot{U}\,\mathrm{d}t \\ &= \int_U^{U_0} \mathrm{d}U \\ \Rightarrow \int_t^{t_0} \mathcal{Q}\,\mathrm{d}t &= U_0 - U \end{aligned} \tag{7}$$

where $U_0 = U(T_0)$ at final time t_0 and $U = U(T)$ at initial time t. For this process, the balance of entropy equation, setting $I_S = -\mathcal{Q}/T_0$ and integrating, gives

$$S_{\text{gen}} = S_0 - S - \frac{1}{T_0}\int_t^{t_0} \mathcal{Q}\,\mathrm{d}t \tag{8}$$

where $S = S(T)$ and $S_0 = S(T_0)$. By substituting Eq. (7) into Eq. (8) we have

$$S_{\text{gen}} = S_0 - S - (1/T_0)(U_0 - U) \tag{9}$$

To write the change of energy in terms of the change in temperature, we simply use the definition for the temperature coefficient of energy:

$$C_V \equiv \frac{\partial U}{\partial T} \tag{10}$$

The entropy generated during the cooling process is then

$$S_{\text{gen}} = S_0 - S - (C_V/T_0)(T_0 - T) \tag{11}$$

Standard thermodynamic relations give the result that

$$\frac{C_V}{T} = \frac{\partial S}{\partial T} \tag{12}$$

so that our final expression for the entropy generated is

$$S_{\text{gen}} = S_0 - S - \left.\frac{\partial S}{\partial T}\right|_0 (T_0 - T) \tag{13}$$

This last expression indicates the concavity property of entropy as a function of T.

Concavity of Entropy

To clarify the meaning of Eq. (13), consider some arbitrary function $F = F(X)$ such that $F'' < 0$. (The inequality indicates that F is a concave function of its argument.) Integrating by parts yields

$$\begin{aligned} -\int_{X_1}^{X_2} &(X - X_1)F''(X)\,\mathrm{d}X \\ &= F(X_2) - F(X_1) - F'(X_2)(X_2 - X_1) \end{aligned} \tag{14}$$

The result on the right-hand side (RHS) has a geometric interpretation, as one can see from Fig. 1, which identifies the RHS of Eq. (13) with the vertical line as shown. Geometrically, we have

$$F(X_2) - F(X_1) - F'(X_2)(X_2 - X_1) \geq 0 \tag{15}$$

where equality holds if and only if $X_2 = X_1$. Comparing Eq. (13) with Eq. (15) demonstrates that, for this case, nonnegative entropy generation, that is, the second law, is equivalent to asserting the concavity property of entropy when $S = S(T)$.

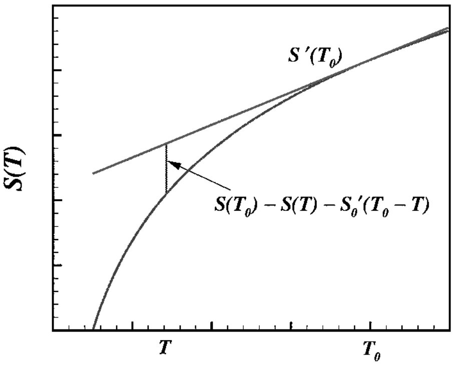

Fig. 1 Entropy: a concave function.

Consider now a simple compressible substance subject to heating $\mathcal{Q}$ and working $\mathcal{W}$, relaxing to equilibrium with an environment at T_0, P_0, where $P_0 = P(T_0, V_0)$. Solving for the heating using the energy balance equation (2) and substituting for the net work done with Eq. (3) gives

$$\int \mathcal{Q}\,\mathrm{d}t = (U_0 - U) + P_0(V_0 - V) \tag{16}$$

The entropy balance then becomes

$$S_{\text{gen}} = S_0 - S - (1/T_0)(U_0 - U) - (P_0/T_0)(V_0 - V) \tag{17}$$

Or, by substituting the appropriate thermodynamic relations and knowing that $S_{\text{gen}} \geq 0$, we can write it as

$$S_0 - S - \left.\frac{\partial S}{\partial T}\right|_0 (T_0 - T) - \left.\frac{\partial S}{\partial V}\right|_0 (V_0 - V) \geq 0 \tag{18}$$

The inequality clearly asserts the concavity of the entropy as a function of T and V.

Therefore, the second general axiom of thermodynamics stipulates the existence of a thermodynamic property called entropy. The mathematical property of concavity asserted by Eq. (18) implies definite restrictions on the constitutive relations for any material body. If we let ξ_k represent the independent variables in the constitutive functional relation such that $U = U(\xi_k)$, $\mathcal{W} = \mathcal{W}(\xi_k)$, etc., then the mathematical property that represents the essence of the second law is

$$\dot{S} - \frac{\partial S}{\partial \xi_k}\dot{\xi}_k \geq 0 \tag{19}$$

Thus, the entropy generated will equal

$$S_{\text{gen}} = \int_{t_1}^{t_2} \dot{S}\,\mathrm{d}t - \int_{t_1}^{t_2} \frac{\partial S}{\partial \xi}\dot{\xi}\,\mathrm{d}t \tag{20}$$

In this paper, the temperature and volume represent the independent variables used in place of ξ. Therefore, mathematically, the concavity property of the entropy as a function of temperature and volume, simply stated, is, where $\exists\, S(T, V) \ni$,

$$\dot{S} - \frac{\partial S}{\partial T}\dot{T} - \frac{\partial S}{\partial V}\dot{V} \geq 0 \tag{21}$$

Using Eqs. (4) and (12) together with $\partial S/\partial V = P/T$ demonstrates that Eqs. (21) and (5) are equivalent because $I_S = \mathcal{Q}/T$ when no mass flows. Thus, the left-hand side (LHS) of Eq. (21) is the entropy generation rate. The mathematical property of concavity of the entropy, therefore, represents the essence of the second law of thermodynamics. Practical consequences such as the various statements for the second law follow, for example, Kelvin–Planck, Clasius's inequality, etc. The cocavity property of entropy translates into a corresponding mathematical property for the exergy, namely, the exergy must be a convex function of its thermodynamic variables.

Concept of Exergy

No thermodynamic system actually exists in perfect isolation. The concavity property of the entropy demonstrates this explicitly, considering that the entropy tends to increase only when deviations from thermal equilibrium with a temperature reservoir occur. In thermodynamics, the concept of exergy was introduced to also address the connection between a system and its environment. Standard textbooks introduce and discuss the subject of availability or exergy in context of the system's potential to do work in a reversible manner. Many modern texts, such as Refs. 16–21 to list a few, also introduce a number of work terms (reversible work, available work, etc.) in an effort to clarify and expand on the subject. However, this often leads to more confusion and quite a bit of cluttering in terminology. This state of affairs was already noted over 20 years ago,[13,14] as was the neglect that availability analysis had suffered. To some degree, the second-law analyses have found well-deserved attention,[7–12] but the cluttering in terminlogy and obscurity in the definitions remains.

Because high-quality energy refers to energy from which we can extract a great deal of useful work, engineers have interpreted exergy as the work potential of that energy. Low-quality energy can produce less work and, therefore, reflects also lower exergy. Thus, exergy quantifies a qualitative aspect of energy. In standard practice, to derive an equation representing the balance of exergy, one typically considers a closed system at some uniform arbitrary state (P, T) relative to the ambient conditions at (P_0, T_0). To measure the distance of our system from the reference or so-called dead state, imagine a reversible process whereby the system relaxes to thermodynamic equilibrium with the surroundings. The energy balance equation simplifies to

$$U_{\mathrm{in}} - U_{\mathrm{out}} = \Delta U \tag{22}$$

where we represent the total change in energy as

$$\Delta U = U(t_2) - U(t_1) = \int_t^{t_0} \dot U \,\mathrm{d}t \tag{23}$$

A closed system relaxes to equilibrium with its surroundings only through heating and working. Integrating the balance of energy equation including heating and working gives

$$\int_t^{t_0} \mathcal{Q}\,\mathrm{d}t + \int_t^{t_0} \mathcal{W}\,\mathrm{d}t = \Delta U \tag{24}$$

with the integral limits defined as the initial time where the system is at (P, T) and the final time when the system has reached equilibrium with the surroundings at (P_0, T_0). To replace the heat interaction term with a state variable, one can use the definition of entropy

$$\int \dot S\,\mathrm{d}t = \frac{1}{T_0}\int \mathcal{Q}\,\mathrm{d}t \Rightarrow T_0\,(S_0 - S) = \int \mathcal{Q}\,\mathrm{d}t \tag{25}$$

To evaluate the work term, it is traditionally recognized that energy quality directly relates to the useful work extracted: the maximum amount of work done during a thermodynamically reversible process. For a simple compressible substance, for which Eq. (3) applies, we have

$$\int \mathcal{W}\,\mathrm{d}t = -\int P\dot V\,\mathrm{d}t = -\underbrace{\int (P - P_0)\dot V\,\mathrm{d}t}_{W_{\mathrm{useful}}} - P_0\int \dot V\,\mathrm{d}t \tag{26}$$

The first term on the RHS defines the maximum useful work available and the second term represents the work done due to the ambient pressure acting on a moving boundary. By substitution of Eqs. (25) and (26) into Eq. (24), we get

$$T_0(S_0 - S) - W_{\mathrm{useful}} - P_0(V_0 - V) = U_0 - U \tag{27}$$

where the subscripts indicate the value at the reference conditions. Solving for the useful work term gives

$$W_{\mathrm{useful}} = T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \tag{28}$$

This defines the exergy X:

$$X \equiv T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \tag{29}$$

Dividing by the total mass gives the specific exergy:

$$\phi \equiv T_0(s_0 - s) - (u_0 - u) - P_0(v_0 - v) \tag{30}$$

Generalizing to include kinetic and gravitational potential energy requires only that we replace u with e, the total specific energy given by $e = u + \frac{1}{2}\mathcal{V}^2 + gz$. Typically, $\mathcal{V}_0 = 0$ and $z_0 = 0$ at the reference state.

Balance of Exergy for Control Mass

With the exergy defined thusly, one can study the change in exergy when the state of a system changes. As a system undergoes a process from one thermodynamic state to another, a corresponding change in exergy occurs. Combining the first and second laws as expressed in the energy and entropy balance equations for a compressible substance of fixed mass results in the balance equation for exergy. In integral form the first and second laws become, for $\mathcal{L}_1$,

$$\int \mathcal{Q}\,\mathrm{d}t + \int \mathcal{W}\,\mathrm{d}t = U_2 - U_1 \tag{31}$$

and for $\mathcal{L}_2$,

$$\int \frac{\mathcal{Q}}{T}\,\mathrm{d}t + S_{\mathrm{gen}} = S_2 - S_1 \tag{32}$$

Combining by taking $\mathcal{L}_1 - T_0\mathcal{L}_2$ gives

$$\int \mathcal{Q}\,\mathrm{d}t + \int \mathcal{W}\,\mathrm{d}t - T_0\int \frac{\mathcal{Q}}{T}\,\mathrm{d}t - T_0 S_{\mathrm{gen}} = U_2 - U_1 - T_0(S_2 - S_1) \tag{33}$$

Collecting terms and replacing the RHS with equivalent terms using the definition of exergy gives

$$\int \left(1 - \frac{T_0}{T}\right)\mathcal{Q}\,\mathrm{d}t + \int \mathcal{W}\,\mathrm{d}t - T_0 S_{\mathrm{gen}} = X_2 - X_1 - P_0(V_2 - V_1) \tag{34}$$

Rearranging by collecting all of the work terms gives

$$\int \left(1 - \frac{T_0}{T}\right)\mathcal{Q}\,\mathrm{d}t + \left\{\int \mathcal{W}\,\mathrm{d}t + P_0(V_2 - V_1)\right\} - T_0 S_{\mathrm{gen}} = X_2 - X_1 \tag{35}$$

Other than a difference in sign on the work term, Eq. (35) is what one typically finds in textbooks on elementary thermodynamics for example, Ref. 16, page 444. If we identify the first term on the left as exergy transfer due to heat interaction in the same sense that we identify entropy transfer due to heat interactions, and the second term (in brackets) as the exergy transfer due to work interaction, then Eq. (35) reduces to a simple formula:

$$I_X - X_{\mathrm{des}} = \Delta X \tag{36}$$

where I_X is the exergy current due to heating, working, etc., and $X_{\mathrm{des}} = T_0 S_{\mathrm{gen}}$ (the so-called Gouy–Stodola identity[22]). Because we associate exergy with work potential, this term is often described as exergy degeneration or a loss of potential work due to real-world, irreversible effects. However, because neither entropy nor exergy are material substances per se, one would probably do better by referring to the quantity expressed by X_{des} as the distance by which the system approached thermodynamic equilibrium with its environment. Recognizing that the second law as expressed in the principle of entropy increase, we require that

$$T_0 S_{\mathrm{gen}} \begin{cases} > 0 & \text{real world} \\ = 0 & \text{ideal world} \\ < 0 & \text{impossible} \end{cases} \tag{37}$$

Because we have associated exergy as equivalent to a measure of work potential, this term can be described as exergy degeneration or a loss of potential work due to real-world, irreversible effects. Therefore, entropy generation results in a corresponding destruction of exergy:

$$X_{\mathrm{des}} = T_0 S_{\mathrm{gen}} \tag{38}$$

Thus, in essence, a system in the real world undergoes spontaneous process that bring it closer to thermodynamic equilibrium with its surroundings. Perhaps this may reflect a more useful interpretation of the second law, in its exergy formulation at least, rather than the often-used terminology of production or destruction of an abstract concept. Regardless, Eq. (38) finds a very powerful application in analyzing complex engineering systems by identifying and minimizing the use of devices or processes that generate entropy.[23]

Balance of Exergy for Control Volume

During an unsteady process where a substance goes from an initial (inlet) to a final (exit) state, the quality of the energy changes, and a corresponding change in its thermodynamic distance from equilibrium occurs. Combining the first and second laws as expressed in the energy and entropy balance equations for an unsteady process, one may obtain the balance equation for exergy. Therefore, representing the first law as

$$\sum \mathcal{Q}_k + \mathcal{W} + \sum \dot{m}\left(h + \frac{1}{2}\mathcal{V}^2 + gz\right)_{\mathrm{in}} - \sum \dot{m}\left(h + \frac{1}{2}\mathcal{V}^2 + gz\right)_{\mathrm{out}} = \dot{E}_{\mathrm{CV}} \tag{39}$$

and the second law as

$$\sum \frac{\mathcal{Q}_k}{T_k} + \sum \dot{m}s\bigg|_{\mathrm{in}} - \sum \dot{m}s\bigg|_{\mathrm{out}} + \dot{S}_{\mathrm{gen}} = \dot{S}_{\mathrm{CV}} \tag{40}$$

we may combine them by taking $\mathcal{L}_1 - T_0\mathcal{L}_2$ to get

$$\sum\left(1 - \frac{T_0}{T}\right)\mathcal{Q}_k + \mathcal{W} + \sum \dot{m}\left(h + \frac{1}{2}\mathcal{V}^2 + gz\right)_{\mathrm{in}} - \sum \dot{m}\left(h + \frac{1}{2}\mathcal{V}^2 + gz\right)_{\mathrm{out}} - T_0\dot{S}_{\mathrm{gen}} = \frac{\mathrm{d}}{\mathrm{d}t}(E - T_0 S)_{\mathrm{CV}} \tag{41}$$

If we define a specific flow exergy ψ in the same sense that enthalpy represents a flow energy, then we can simplify the exergy balance equation to

$$\sum\left(1 - \frac{T_0}{T}\right)\mathcal{Q}_k + (\mathcal{W} + P_0\dot{V}) + \sum \dot{m}\psi_{\mathrm{in}} - \sum \dot{m}\psi_{\mathrm{out}} - T_0\dot{S}_{\mathrm{gen}} = \dot{X}_{\mathrm{CV}} \tag{42}$$

where

$$\psi = \phi + (P - P_0)v \tag{43}$$

and $P_0\dot{V}$ appears once we replace the RHS of Eq. (42) with the equivalent terms from Eq. (29) and move the extra term to the LHS. Identifying the first two terms on the left of Eq. (42) as the transfer of exergy due to heating and working, respectively, and the third and fourth terms as exergy transfer due to mass flow, the exergy balance equation for a control volume process reduces to

$$\dot{X}_{\mathrm{in}} - \dot{X}_{\mathrm{out}} - T_0\dot{S}_{\mathrm{gen}} = \dot{X}_{\mathrm{CV}} \tag{44}$$

where the in and out terms represent the current of exergy into and out of the control volume.

Second-Law Effectiveness

In addition to its role in determining the direction of spontaneous natural process and as a criterion for thermodynamic equilibrium, the second law can also measure the efficiency of engineering devices. In fact, Carnot[24] conceived and developed the second law to account for the performance and limits of heat engines. Isentropic efficiency compares the quality of various engineering devices such as turbines and compressors. In the context of exergy, the second law defines a more general measure of performance that applies not only to turbines and compressors but to heat exchangers and mixing processes as well. Basically, a measure of performance for any real-world device should compare its efficiency relative to the efficiency of an ideal device (no irreversible losses) operating under the same conditions. Such a measure of performance, called the second-law efficiency or effectiveness, results in the definition

$$\eta_{\mathrm{II}} \equiv 1 - (\dot{X}_{\mathrm{des}}/\dot{X}_{\mathrm{supp}}) \tag{45}$$

The literature also identifies this measure of performance as the rational efficiency of a process or device.[13,14] Essentially, the effectiveness of any process equals the fractional change in the exergy relative to the exergy supplied. Because $\dot{X}_{\mathrm{supp}} = \dot{X}_{\mathrm{in}} - \dot{X}_{\mathrm{out}}$ (i.e., the net exergy current), dividing Eq. (44) by this term gives definition (45). The concept of effectiveness applies to any thermophysical process, including heat engines, refrigerators, heat exchangers, mixing, throttling, etc., and is always bounded by zero and one. The second law of thermodynamics will then 1) determine the direction of change for spontaneous, natural processes, 2) establish criteria for equilibrium in thermodynamic systems, and 3) provide the theoretical limits for the performance of engineering systems and processes. Items 1 and 2 identify the role of the second law as the limiter in abstracting the differences in response of different materials via the constitutive relations. Item 3 identifies the role of the second law enumerated by the concept of effectiveness as a limiter as to how a system may relax to equilibrium conditions with its surroundings while producing or consuming work.

Revised Interpretation and Implications

Thus far we have used only conventional logic and basic methodology as presented by standard, that is, textbook, approaches. For a revised interpretation and analysis, consider again the second law of thermodynamics. The essence of the second law postulates the existence of a functional called the entropy, concave with respect to the other thermodynamic variables. Hence, $\exists\, S(T, V) \ni$,

$$S_0 - S - \frac{\partial S}{\partial T}\bigg|_0 (T_0 - T) - \frac{\partial S}{\partial V}\bigg|_0 (V_0 - V) \geq 0 \tag{46}$$

Equality holds if and only if $(T, V) = (T_0, V_0)$. Thermodynamic relations provide

$$\frac{C_V}{T} = \frac{\partial S}{\partial T}, \qquad \frac{P}{T} = \frac{\partial S}{\partial V} \tag{47}$$

Rewriting the inequality shows that the concavity property, multiplied by the temperature, equals the exergy as defined by Eq. (29):

$$T_0(S_0 - S) - (U_0 - U) - P_0(V_0 - V) \geq 0 \tag{48}$$

where we have replaced $C_V(T_0 - T)$ with $(U_0 - U)$. Writing the balance of entropy as an equation for the entropy generation rate gives

$$\dot{S}_{\mathrm{gen}} = \dot{S} - \frac{\partial S}{\partial T}\dot{T} - \frac{\partial S}{\partial V}\dot{V} \geq 0 \tag{49}$$

As stated, the second law, in essence, reflects the mathematical property contained in Eq. (49), asserting that entropy is a concave function of its thermodynamic arguments. From the definition of exergy, the concavity of the entropy translates directly to a complementary convexity condition on the exergy as a function of its arguments. To demonstrate, consider the definition of exergy given by

$$X = T_0(S_0 - S) - C_V(T_0 - T) - P_0(V_0 - V) \tag{50}$$

in terms of the temperature and volume. Taking the time rate of change, this becomes

$$\dot{X} = -T_0\dot{S} + C_V\dot{T} + P_0\dot{V} \tag{51}$$

From the entropy balance equation (49), we have

$$\dot{S} = \dot{S}_{\text{gen}} + \frac{\partial S}{\partial T}\dot{T} + \frac{\partial S}{\partial V}\dot{V} \tag{52}$$

so that, by substitution of Eq. (52) into Eq. (51), replacing terms defined by Eq. (47), and then collecting terms, we get

$$\dot{X} = -T_0\dot{S}_{\text{gen}} + [1 - (T_0/T)]C_V\dot{T} + [P_0 - T_0(P/T)]\dot{V} \tag{53}$$

Moving the terms in brackets to the LHS gives

$$\dot{X} - [1 - (T_0/T)]C_V\dot{T} - [P_0 - T_0(P/T)]\dot{V} = -T_0\dot{S}_{\text{gen}} \tag{54}$$

From the definition of exergy, we can prove that the following thermodynamic relations hold:

$$\frac{\partial X}{\partial V} = \left(P_0 - T_0\frac{P}{T}\right), \qquad \frac{\partial X}{\partial T} = \left(1 - \frac{T_0}{T}\right)C_V \tag{55}$$

By subsituting these into Eq. (54) and invoking the second law as $\dot{S}_{\text{gen}} \geq 0$, we get

$$\dot{X} - \frac{\partial X}{\partial T}\dot{T} - \frac{\partial X}{\partial V}\dot{V} \leq 0 \tag{56}$$

The inequality in Eq. (56) asserts the mathematical property of convexity for $X = X(T, V)$. Thus, one may formulate the second law as a statement for the existence of a functional called exergy that must be convex in the independent thermodynamic variables chosen. Note that if one of the independent thermodynamic variables chosen is either the entropy or the exergy, then the strict equality holds, and the only way the second law is satisfied is to assert that the thermodynamic, system is in a state of equilibrium. This has been the traditional approach to classical thermodynamics, but the development here demonstrates the generality of the science and of the second law in particular.

For a closed system exchanging energy with its surroundings through heating and working, consider the time-dependent version of the balance of exergy as expressed by Eq. (35):

$$[1 - (T_0/T)]\mathcal{Q} + (\mathcal{W} + P_0\dot{V}) - T_0\dot{S}_{\text{gen}} = \dot{X} \tag{57}$$

Replacing the heating with the RHS of Eq. (2) (the first law) and then working with Eq. (3) (a constitutive relation) gives

$$[1 - (T_0/T)](C_V\dot{T} + P\dot{V}) - P\dot{V} + P_0\dot{V} - T_0\dot{S}_{\text{gen}} = \dot{X} \tag{58}$$

Expanding, canceling, recollecting terms, and simplifying yields the expression

$$\Rightarrow\ [1 - (T_0/T)]C_V\dot{T} + [P_0 - (T_0/T)P]\dot{V} - T_0\dot{S}_{\text{gen}} = \dot{X} \tag{59}$$

Moving the terms in brackets to the RHS,

$$-T_0\dot{S}_{\text{gen}} = \dot{X} - [1 - (T_0/T)]C_V\dot{T} - [P_0 - (T_0/T)P]\dot{V} \tag{60}$$

Using thermodynamic relations (55) for the exergy gradients gives

$$\Rightarrow\ -T_0\dot{S}_{\text{gen}} = \dot{X} - \frac{\partial X}{\partial T}\dot{T} - \frac{\partial X}{\partial V}\dot{V} \tag{61}$$

which is identical to Eq. (56) under the requirement that $\dot{S}_{\text{gen}} \geq 0$. Therefore, one may derive the same result simply by using the direct connection between exergy and the concavity property of the entropy and simply substituting the first and second laws into the resulting expression. We need not resort to any useful work, reversible work, or any other kind of work if only we interpret the meaning of exergy as a thermodynamic metric or distance functional. Mathematically, of course, the requirements for a true metric differ, but conceptually the idea holds.

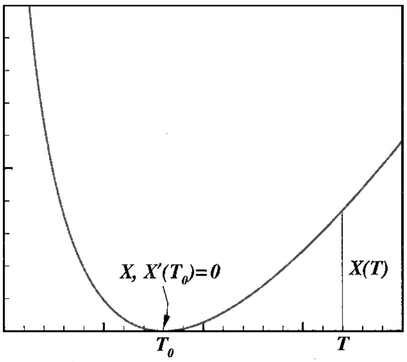

Fig. 2 Exergy: a convex function.

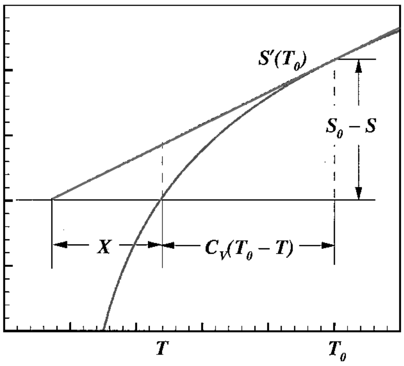

Fig. 3 Geometric representation of exergy.

Geometric Complementarity

The essence of the second law lies in the concavity property of the entropy. This was demonstrated by Lavenda[25] from a probabilistic viewpoint. One can utilize the idea to develop thermodynamics on a phenomenological level as well. Figure 2 shows the exergy as a convex function of temperature. A geometric complementary relation exists between entropy and exergy, as shown by the concavity inequality for the entropy and identifying the segment that defines exergy. This is shown in Fig. 3. The definition of exergy makes it clear that it has an absolute minimum at the point of equilibrium. The tangent slope at this point coincides with the horizontal axis of zero exergy. The straight vertical line from the arbitrary initial state indicated in Fig. 2 represents the corresponding distance to equilibrium. The distance to equilibrium is represented equally well by the vertical line shown in Fig. 1 (concavity of the entropy) or the horizontal line in Fig. 2 (geometric representation of exergy).

Mathematical Metric

To restate, we need not resort to any useful work, reversible work, or any other kind of work if only we interpret the meaning of exergy as a thermodynamic metric or distance functional. Mathematically, of course, the requirements for a true metric differ but conceptually the idea holds. If one insists on satisfying the mathematical requirements, however, we can still define a metric based on the Hessian of the entropy (a second-order tensor of derivatives with respect to the thermodynamic variables). This allows the construction of the inner product

$$(\boldsymbol{x}, \boldsymbol{x}) \equiv \boldsymbol{x}^T \cdot (-\boldsymbol{S}_{xx})_0 \cdot \boldsymbol{x} \tag{62}$$

where

$$(\boldsymbol{S}_{xx})_0 = \begin{bmatrix} \dfrac{\partial^2 S}{\partial T^2} & \dfrac{\partial^2 S}{\partial T \partial V} \\ \dfrac{\partial^2 S}{\partial T \partial V} & \dfrac{\partial^2 S}{\partial V^2} \end{bmatrix}_0 \tag{63}$$

represents the Hessian and

$$\boldsymbol{x}^T \equiv (T, V) \tag{64}$$

represents an algebraic vector of the corresponding thermodynamic variables. The inner product (62) results in nonnegative values as guaranteed by the concavity property of entropy. A true mathematical metric may then be defined by the distance functional

$$\|\boldsymbol{x} - \boldsymbol{x}_0\| \equiv (\Delta\boldsymbol{x}, \Delta\boldsymbol{x})^{\frac{1}{2}} \tag{65}$$

where $\Delta\boldsymbol{x} = \boldsymbol{x} - \boldsymbol{x}_0$.

To clarify the meaning of Eq. (62) and its relation to exergy, consider the construction of the norm $\|x\|$, which requires evaluation of the second derivative terms of the Hessian (63). Thermodynamic relations from Table 4.6 of Ref. 22, page 183, give

$$\frac{\partial^2 S}{\partial T^2} = -\frac{C_V}{T^2} \tag{66}$$

$$\frac{\partial^2 S}{\partial T \partial V} = -\frac{1}{\kappa T^2}(\kappa P - \beta T) \tag{67}$$

$$\frac{\partial^2 S}{\partial V^2} = -\frac{1}{\kappa T^2}\left(\frac{\kappa P^2 - 2\beta TP}{C_V} + \frac{C_P T}{C_V V}\right) \tag{68}$$

where

$$\beta \equiv \frac{1}{V}\frac{\partial V}{\partial T} \tag{69}$$

$$\kappa \equiv -\frac{1}{V}\frac{\partial V}{\partial P} \tag{70}$$

represent the volumetric coefficients of thermal expansion and isothermal compressibility, respectively. With these definitions, the Hessian reduces to

$$\boldsymbol{S}_{xx} = \frac{-1}{\kappa T^2}\begin{bmatrix} \kappa C_V & \kappa P - \beta T \\ \kappa P - \beta T & \dfrac{\kappa P^2 - 2\beta TP}{C_V} + \dfrac{C_P}{C_V}\dfrac{T}{V} \end{bmatrix}$$

which gives the inner product

$$(\boldsymbol{x}, \boldsymbol{x}) = (1/\kappa C_V T_0)\left\{(\kappa H^2/T_0) - 2\beta HV + (C_P V^2/V_0)\right\} \tag{71}$$

where we use $H = C_V T + P_0 V$ to simplify the result. To demonstrate that Eq. (62) gives nonnegative values, consider two extreme cases: that of an ideal gas and an incompressible substance. For an ideal gas,

$$\kappa P = 1, \qquad \beta T = 1 \tag{72}$$

and the inner product simplifies to

$$(\boldsymbol{x}, \boldsymbol{x}) = C_V\left(\frac{T}{T_0}\right)^2 - \frac{P_0^2 V^2}{C_V T_0^2} + \frac{C_P P_0 V^2}{C_V T_0 V_0} \tag{73}$$

To simplify further, one can use the ideal gas equation of state

$$PV = \hat{R}T \tag{74}$$

together with the relations

$$C_V = \hat{R}/(\gamma - 1), \qquad C_P = \gamma\hat{R}/(\gamma - 1), \qquad \gamma \equiv C_P/C_V \tag{75}$$

By substitution and simplification, one obtains

$$(\boldsymbol{x}, \boldsymbol{x}) = \hat{R}/(\gamma - 1)(T/T_0)^2 + \hat{R}(V/V_0)^2 \tag{76}$$

where $\hat{R} = m\mathcal{R}/M$. Respectively, m, M, and $\mathcal{R}$ equal the mass, molecular weight, and the universal gas constant. The subscripts denote reference conditions for the pressure and temperature. Replacing (U, V) with the corresponding differences $(U - U_0, V - V_0)$ yields the square of a true mathematical distance functional,

$$\|\boldsymbol{x}_0 - \boldsymbol{x}\|^2 = \hat{R}/(\gamma - 1)(1 - T/T_0)^2 + \hat{R}(1 - V/V_0)^2 \tag{77}$$

Following the same procedure for an incompressible substance, where κ, $\beta \longrightarrow 0$, and C_P, $C_V \longrightarrow C$, will show that Eq. (71) reduces to

$$\|\boldsymbol{x}_0 - \boldsymbol{x}\|^2 = C(1 - T/T_0)^2 \tag{78}$$

Thus, by expanding the idea of distance to allow for the interpretation of exergy as a thermodynamic distance functional, we can eliminate much of the confusion that arises when one refers to the multiple kinds of work. To strengthen the case, let us connect the mathematical distance functional as derived with the concept of exergy. Consider a system near equilibrium conditions and expand the entropy function in a Taylor's series. Dropping higher than second-order terms will yield

$$S \approx S_0 + \left.\frac{\partial S}{\partial T}\right|_0 (T - T_0) + \left.\frac{\partial S}{\partial V}\right|_0 (V - V_0) + \frac{1}{2}(\boldsymbol{x} - \boldsymbol{x}_0)^T \cdot \boldsymbol{S}_{xx}|_0 \cdot (\boldsymbol{x} - \boldsymbol{x}_0) \tag{79}$$

Rearranging and using the definition of exergy as prescribed in Eq. (50) easily shows that

$$X \approx \tfrac{1}{2}T_0\|\boldsymbol{x} - \boldsymbol{x}_0\|^2 \tag{80}$$

A systematic development of the concept of exergy directly from the concavity property of entropy thus leads to a more mathematically rigorous approach than relying on multiple definitions of work. Equation (80) proves that the exergy does indeed represent an abstract measure of the distance from equilibrium conditions for a system at some arbitrary state.

Sometimes thermodynamic relations are developed using the extensive variables of energy and volume as independent. In this case, consider $S(U, V)$ as the entropy functional dependent on energy and volume. Then

$$(\boldsymbol{S}_{,xx})_0 = \begin{bmatrix} \dfrac{\partial^2 S}{\partial U^2} & \dfrac{\partial^2 S}{\partial U \partial V} \\ \dfrac{\partial^2 S}{\partial U \partial V} & \dfrac{\partial^2 S}{\partial V^2} \end{bmatrix}_0 \tag{81}$$

represents the Hessian and $\boldsymbol{x}^T \equiv (U, V)$ equals an algebraic vector of the corresponding extensive thermodynamic variables. Thermodynamic relations again from Table 4.6 in Ref. 22, page 183, give

$$\frac{\partial^2 S}{\partial U^2} = -\frac{1}{C_V T^2} \tag{82}$$

$$\frac{\partial^2 S}{\partial U \partial V} = -\frac{1}{\kappa C_V T^2}(\kappa P - \beta T) \tag{83}$$

$$\frac{\partial^2 S}{\partial V^2} = -\frac{1}{\kappa C_V T^2}\left(\kappa P^2 - 2\beta TP + \frac{C_P T}{V}\right) \tag{84}$$

which reduce the Hessian to

$$\boldsymbol{S}_{xx} = \frac{-1}{\kappa C_V T^2}\begin{bmatrix} \kappa & \kappa P - \beta T \\ \kappa P - \beta T & \kappa P^2 - 2\beta TP + (C_P T/V) \end{bmatrix}$$

which, in turn, gives the inner product

$$(\boldsymbol{x}, \boldsymbol{x}) = (1/\kappa C_V T_0)\left\{\kappa H^2/T_0 - 2\beta HV + C_P V^2/V_0\right\} \tag{85}$$

where $H = U + P_0V$ simplifies the result. For an ideal gas, setting $\kappa P = 1$ and $\beta T = 1$ simplifies Eq. (85) to

$$(\boldsymbol{x}, \boldsymbol{x}) = (1/C_V T_0^2)\left\{U^2 - (P_0V)^2 + C_P T_0 P_0 (V^2/V_0)\right\} \tag{86}$$

By substitution and simplification of the ideal gas relations (74) and (75), one obtains

$$(\boldsymbol{x}, \boldsymbol{x}) = (1/\hat{R}T_0^2)\left\{(\gamma - 1)U^2 + P_0^2 V^2\right\} \tag{87}$$

Replacing (U, V) with $(U - U_0, V - V_0)$ yields the square of the mathematical distance functional,

$$\|\boldsymbol{x}_0 - \boldsymbol{x}\|^2 = (\gamma - 1)/\hat{R}T_0^2 (U_0 - U)^2 + (P_0^2/\hat{R}T_0^2)(V_0 - V)^2 \tag{88}$$

Following the same procedure for an incompressible substance will show that

$$\|\boldsymbol{x}_0 - \boldsymbol{x}\|^2 = \frac{(U_0 - U)^2}{CT_0^2} \tag{89}$$

Consider again a system near equilibrium conditions and expand the entropy function in a Taylor's series. Dropping higher than second-order terms will yield

$$S \approx S_0 + \left.\frac{\partial S}{\partial U}\right|_0 (U - U_0) + \left.\frac{\partial S}{\partial V}\right|_0 (V - V_0) + \frac{1}{2}(\boldsymbol{x} - \boldsymbol{x}_0)^T \cdot \boldsymbol{S}_{xx}|_0 \cdot (\boldsymbol{x} - \boldsymbol{x}_0) \tag{90}$$

Rearranging and using the definition of exergy as prescribed in Eq. (48) shows immediately that

$$X \approx \tfrac{1}{2} T_0 \|\boldsymbol{x} - \boldsymbol{x}_0\|^2 \tag{91}$$

A systematic development of the concept of exergy directly from the concavity property of entropy leads to a more mathematically rigorous approach than relying on multiple definitions of work.

Continuum Thermomechanics

Thus far, only classical thermodynamics have been discussed. The ideas presented here also generalize to establish the fundamentals of continuum thermomechanics, which would express the physical principles mathematically as

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho \mathcal{V}_j}{\partial x_j} = 0 \tag{92}$$

$$\frac{\partial \rho \mathcal{V}_i}{\partial t} + \frac{\partial}{\partial x_j}(\rho \mathcal{V}_j \mathcal{V}_i + P\delta_{ji} - \tau_{ji}) = 0 \tag{93}$$

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j}[E\mathcal{V}_j + P\mathcal{V}_j - \tau_{ji}\mathcal{V}_i + q_j] = 0 \tag{94}$$

where $E = \rho u + \frac{1}{2}\rho \mathcal{V}^2$ represents the total energy density. The fluid mechanics literature identifies Eqs. (92–94) as the Navier–Stokes equations. Mathematically, these equations are complete but underdetermined in the sense that they contain more unknown variables than equations. One needs additional information before solving any problem in fluid mechanics. The constitutive relations provide that additional closure information. Typically, these include the ideal gas law,

$$P = \rho RT \tag{95}$$

the assumption of a thermally perfect gas (c_v depends only on the temperature T),

$$u = c_v T \tag{96}$$

Fourier's relation for heat conduction,

$$q_j = -k\frac{\partial T}{\partial x_j} \tag{97}$$

and a formula for the viscous stress tensor,

$$\tau_{ji} = \mu\left(\frac{\partial \mathcal{V}_j}{\partial x_i} + \frac{\partial \mathcal{V}_i}{\partial x_j}\right) + \lambda \frac{\partial \mathcal{V}_j}{\partial x_j}\delta_{ji} \tag{98}$$

In addition, one would need the balance of entropy equation extended to the continuum. From Eq. (5), the generalized entropy balance equation becomes

$$\dot{S}_{\text{gen}} = \frac{\partial S}{\partial t} + \frac{\partial S\mathcal{V}_j}{\partial x_j} + \frac{\partial}{\partial x_j}\left(\frac{q_j}{T}\right) \tag{99}$$

where $S = \rho s$. The inequality $\dot{S}_{\text{gen}} \geq 0$ would impose restrictions on the heating term as well as the viscous dissipation; both are constitutive relations. Because one more unknown has been added, another constitutive relation is needed, namely, the functional formula for the entropy in terms of the other field variables. This functional relation must satisfy the concavity property of the entropy, which is essential in formulating the second law. For an ideal gas, the entropy functional, written in nondimensional form, is

$$s(\rho, T) = 1/(\gamma - 1)\ln T - \ln \rho \tag{100}$$

Because the state variables include the mass, momentum, and total energy densities, it is reasonable to define an algebraic vector $\boldsymbol{Q}^T \equiv \{\rho,\ \rho\mathcal{V}_1,\ \rho\mathcal{V}_2,\ \rho\mathcal{V}_3,\ \rho E\}$ so that the entire set of equations (92–94) reduce to

$$\frac{\partial \boldsymbol{Q}}{\partial t} + \frac{\partial \boldsymbol{F}_k}{\partial x_k} = 0 \tag{101}$$

The functional relation for the entropy is then $S = S(\boldsymbol{Q})$, and one may verify the concavity property by writing

$$S_0 - S - \left.\frac{\partial S}{\partial \boldsymbol{Q}}\right|_0 \cdot (\boldsymbol{Q}_0 - \boldsymbol{Q}) \geq 0 \tag{102}$$

where equality holds if and only if $\boldsymbol{Q} = \boldsymbol{Q}_0$, that is, the fluid rests at equilibrium conditions. Following the logic outlined earlier, the concavity property tranforms into a convexity condition on the exergy, now defined as

$$X(\boldsymbol{Q}) \equiv T_0\left[S_0 - S - \left.\frac{\partial S}{\partial \boldsymbol{Q}}\right|_0 \cdot (\boldsymbol{Q}_0 - \boldsymbol{Q})\right] \tag{103}$$

in the same sense that Eq. (48) was derived from Eq. (46).

In addition, because it was demonstrated that the concavity property of the entropy is equivalent to the balance of entropy equation, one can show that concavity as expressed by Eq. (102) lies buried in the balance of entropy equation (99). The time rate of change version of Eq. (102) is the extension of Eq. (19):

$$\dot{S}_{\text{gen}} = \frac{\mathrm{d}S}{\mathrm{d}t} - \frac{\partial S}{\partial \boldsymbol{Q}} \cdot \frac{\mathrm{d}\boldsymbol{Q}}{\mathrm{d}t} \geq 0 \tag{104}$$

where the time derivatives are now total. By definition, $\dot{S}_{\text{gen}} = \mathrm{d}S/\mathrm{d}t$, and the conservation law form for the balance equation equates $\mathrm{d}\boldsymbol{Q}/\mathrm{d}t$ with Eq. (101), which equals zero. Thus, Eq. (104) is satisfied identically, but this is not a trivial result because if we replace $\mathrm{d}S/\mathrm{d}t$ with the RHS of Eq. (99) and $\mathrm{d}\boldsymbol{Q}/\mathrm{d}t$ with Eq. (101), we obtain

$$\dot{S}_{\text{gen}} = \frac{\partial S}{\partial t} + \frac{\partial S\mathcal{V}_j}{\partial x_j} + \frac{\partial}{\partial x_j}\left(\frac{q_j}{T}\right) - \frac{\partial S}{\partial \boldsymbol{Q}} \cdot \frac{\partial \boldsymbol{Q}}{\partial t} - \frac{\partial S}{\partial \boldsymbol{Q}} \cdot \frac{\partial \boldsymbol{F}_k}{\partial x_k} \tag{105}$$

The chain rule of differentiation cancels the time derivative terms. In addition, although the details are omitted but verified readily, the last term in Eq. (105) expands to

$$\frac{\partial S}{\partial \boldsymbol{Q}} \cdot \frac{\partial \boldsymbol{F}_k}{\partial x_k} = \frac{\partial S\mathcal{V}_j}{\partial x_j} + \frac{\partial}{\partial x_j}\left(\frac{q_j}{T}\right) - \frac{1}{T}\tau_{ji}\frac{\partial \mathcal{V}_i}{\partial x_j} + \frac{q_j}{T^2}\frac{\partial T}{\partial x_j} \tag{106}$$

For details (in the one-dimensional case), see the author's paper.[26] The entropy generation rate shows the explicit effects of dissipation and heat conduction:

$$\dot{S}_{\text{gen}} = \frac{\tau_{ji}}{T}\frac{\partial \mathcal{V}_i}{\partial x_j} - \frac{q_j}{T^2}\frac{\partial T}{\partial x_j} \tag{107}$$

This result may be obtained by other means (e.g., Ref. 2, page 17) but the approach taken here emphasizes the deep connection between the concavity property of the entropy functional and what classical thermodynamics claimed as the entropy generation equation or the second law of thermodynamics.

Assuming the Fourier heat-conduction relation, together with the formula for the viscous stress tensor, the second law requires that

$$k \geq 0, \qquad \mu \geq 0, \qquad \lambda + \tfrac{2}{3}\mu \geq 0 \tag{108}$$

These results are known in the advanced literature dealing with thermodynamics and kinetic theory.[1–3] Here we stress that the origin of these inequalities comes from the mathematical property of entropy concavity as a function of the field variables. The utility of the second law clearly makes itself evident: It links the general principles of physics that model natural phenomena to the constitutive relations that idealize the response of material bodies subject to those principles. This work attempted to place the concept of entropy, the second law, and the concept of exergy squarely in the realm of mathematical (probabilistic) logic, as envisioned by Jaynes in Ref. 27, making it a fundamental principle expressive of its true potential and power.

Conclusions

The power and generality of the second law of thermodynamics have always been evident in at least three capacities: 1) for the determination of the direction of change for spontaneous, natural processes, 2) for establishing criteria for equilibrium in thermodynamic systems, and 3) for providing the theoretical limits for the performance of engineering systems. Many generalized approaches have been developed to extend the power of the second law in terms of exergy. However, the essential core of the second law has not always been evident. This work attempts to highlight the peculiar mathematical property intrinsic to the second law by showing that the concavity property of the entropy translates directly into a convexity requirement on the exergy. A systematic development of the concept of exergy directly from the concavity property of entropy then leads to a more mathematically rigorous approach than relying on multiple definitions of work. Equations (80) and (91) proved that the exergy does indeed represent an abstract measure of the distance from equilibrium conditions for a system at some arbitrary state. The preceding section generalized the ideas to continuum thermomechanics, but this rough development requires further elaboration and will remain a future task perhaps to be presented elsewhere.

The second law has deep and practical implications in engineering science. As machines become increasingly complex and sophisticated in their ability to transform energy into forms useful to humankind, the second law will play an equally increasing role in prescribing their limits of performance. Since the industrial revolution, the second law played only a secondary role by grossly prescribing what the real physical world allowed. Machines of the future will require a more delicate and intimate relationship as we press toward the limits of engineering design, precisely where the true power of the second law becomes evident. It stands to reason, therefore, that engineers and scientists fully understand what the second law, entropy, and exergy tell us about the real world and our limited mathematical representations of it. Systematically developing the foundations of the second law from the essence of entropy as a concave function of the state variables, we advance that idea together with a simplicity that will make it possible for future engineers and scientists to achieve what we can now only imagine.

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