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Classical Thermodynamics Revisited

A SYSTEMS
AND CONTROL
PERSPECTIVE

ARJAN VAN DER SCHAFT

Thermodynamics has been the subject of intense scientific debate throughout its long history (see “Summary”). The following famous quote from Albert Einstein’s autobiographical notes expresses his admiration for the theory of classical, macroscopic thermodynamics [1]:

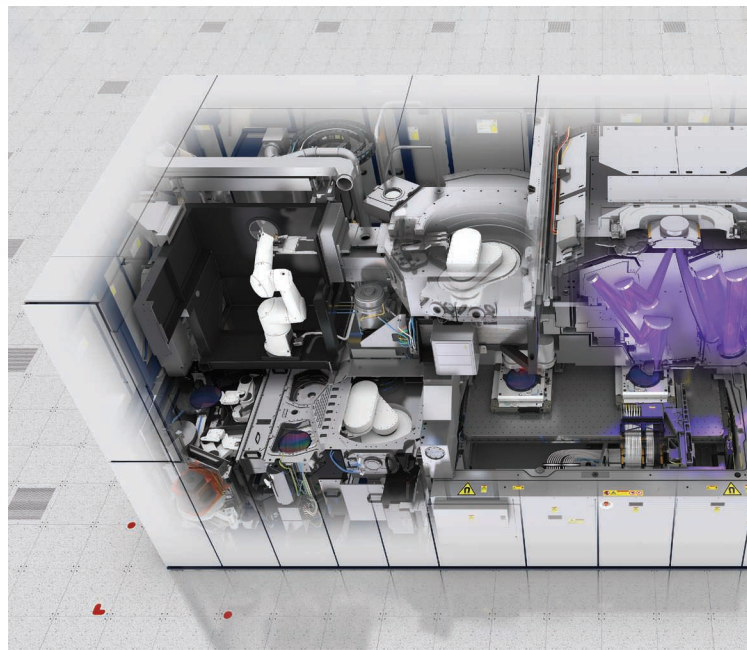
A theory is more impressive the greater the simplicity of its premises, the more different things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

On the other hand, there are other (and less favorable) opinions. The eminent Russian mathematician Vladimir I. Arnold stated [2]

Every mathematician knows that it is impossible to understand any elementary course in thermodynamics. The reason is that the thermodynamics is based,—as Gibbs has explicitly proclaimed—, on a rather complicated mathematical theory, on the contact geometry.

Although Arnold attributed the difficulty in understanding thermodynamics to an inherent mathematical difficulty, others often criticized the imprecise and mathematically outdated presentation of thermodynamics. The perhaps most salient opinion in this regard was expressed by the American mathematician and natural philosopher Clifford Truesdell, who described the formulation of the theory of thermodynamics as a “dismal swamp of obscurity” [3, p. 6]. Quoting from [4], in a desperate attempt to try to make sense of the writings of De Groot et al., he (Truesdell) goes on to state that there is [5, p. 134] “something rotten in the (thermodynamic) state of the Low Countries.” Clearly, the author of the present article feels addressed by this last statement.

The purpose of this article is to make clear (and demystify) the basic concepts of classical thermodynamics from a systems and control perspective. The purpose is also to argue that systems and control theory provides a natural context for the formulation and understanding of classical thermodynamics. This is not so surprising, as historically, classical thermodynamics is firmly rooted in (control) engineering

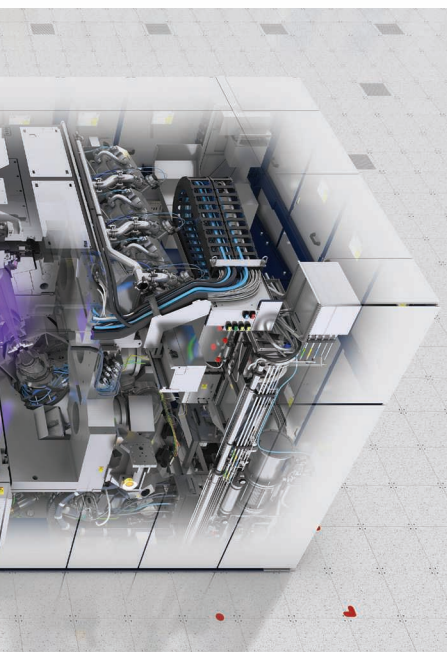


problems such as the maximal efficiency of steam engines. Furthermore, thermodynamics deals from the very start with systems in interaction with their surroundings (by heat flow, mechanical work, and flow of matter). As shown later, there are many points of close contact between thermodynamics on the one hand and systems and control on the other. In particular, (cyclo-)dissipativity theory (as founded by Willems in [6], with thermodynamics as one of its motivations) is key to the formulation and interpretation of the first and second law of thermodynamics. Furthermore, it provides the right angle to the understanding of

the classical Carnot cycle, the interpretation of Clausius' inequality, and a clear macroscopic definition of entropy. Conversely, thermodynamics motivates challenging control problems, such as the (maximal) conversion of one type of energy into another. Another emphasis of this article, in line with (nonlinear) geometric control, is the geometric (coordinate-free) view on the state properties and dynamics of thermodynamic systems, thereby unifying different representations and facilitating their structural analysis (such as controllability and observability).

Thermodynamics also motivates paradigm shifts within systems and control; in particular, the use of nonminimal state-space formulations. Furthermore, although systems and control theory has been primarily based on linear systems with quadratic cost criteria (in line with basic system models in electrical and mechanical engineering, such as RLC-circuits and mass-spring-damper systems), thermodynamics necessitates going beyond this linear-quadratic paradigm. Finally, from a direct control applications perspective, thermodynamics has always been important in chemical engineering and related areas. Deal-

ing with thermal behavior is becoming highly important in many other advanced engineering problems as well (for example, thermal deformations in high-precision systems, smart materials, and general control problems in energy harvesting and conversion). Although the present article does not explicitly address such problems, it paves the way for incorporating (in a natural and unified way) thermodynamics in systems modeling and control frameworks for solving such control problems.



ASML, THE NETHERLANDS

WHAT THIS ARTICLE IS NOT ABOUT

Thermodynamics is a theory relating many areas in the physical sciences, from gases, and chemical reactions, to radiation [7]–[9] (in accordance with the aforementioned quote by Albert Einstein on the universality of thermodynamics). The present article is *not* about all these different application areas, and the presented examples are simple and do *not* illustrate the power and intricacies of the theory when applied to complex physical situations. Instead, this article confines itself to the conceptual and mathematical structure of the theory of classical thermodynamics, as seen from a

Summary

From its very start, thermodynamics has been motivated by engineering questions such as the maximal efficiency of engines for converting heat into work. Furthermore, thermodynamics considers systems that are in interaction with their surroundings by heat flow, mechanical work, flow of matter, and so on. Hence, it may not come as a surprise that classical, macroscopic thermodynamics can be naturally understood from a systems and control perspective. In particular, the first and second laws of thermodynamics are rightfully formulated using cyclo-dissipativity theory, with energy and entropy appearing as storage functions. Next, the extensive variables, including energy and entropy, together with the intensive variables such as temperature and pressure, define a nonminimal state space, called the thermodynamic phase space. The constitutive properties of any thermodynamic system are specified by a subset of this thermodynamic phase space with natural geometric properties. Dynamics respects the geometry of the thermodynamic phase space and leaves invariant the subset specifying the constitutive properties. This geometrization is essential for the integration of thermodynamics within modern frameworks for modeling and control of complex multiphysics systems. In particular, it provides the theory for addressing advanced engineering problems in, for example, high-precision systems, smart materials, chemical engineering, and general control problems in energy harvesting and conversion.

systems and control perspective. Furthermore, the article concentrates on *macroscopic* thermodynamics, without making any connection to statistical physics, or middle-ground theories, as in [10]. This is a part of the beauty and power of classical, macroscopic, thermodynamics: it can be presented as a self-contained theory, purely based on macroscopic quantities and the postulates of the first and second law. Only in “Other Views on Entropy” will the connections to other definitions of entropy be briefly noted. Moreover, the article is about the lumped-parameter case, although much is extendable to mesoscopic (that is, in between macroscopic and microscopic) thermodynamics. Also, no attempt was made to provide a balanced view of the large amount of literature on the subject (see [7], [9], and [10] for a wealth of references). Finally, the article reflects the author’s personal journey in understanding classical thermodynamics from a systems and control perspective, and as such inevitably presents a biased view on this multifaceted subject.

Basic Terminology

A possible obstacle in understanding classical thermodynamics is the terminology used. This section aims to explain, in an informal manner and without claiming full

Other Views on Entropy

In “The Second Law of Thermodynamics” section, the classical way of defining entropy (going back to Clausius and rooted in the Carnot cycle) is discussed. As shown, this definition of entropy (based on Clausius’ inequality) allows for a natural formulation within cyclo-dissipativity theory. Furthermore, the Carnot cycle has a control engineering motivation of optimal conversion of heat into work. Other developments within thermodynamics have moved away from this engineering background. A crucial development is the definition of entropy from a statistical and microscopic perspective (as given by Boltzmann and Gibbs and briefly discussed at the end of this section). Another approach, within classical thermodynamics, was initiated by Carathéodory and advocated by Born. The basic idea is as follows [S1]. Consider a simple thermodynamic system (the argument can be quite easily extended to more complicated situations). By the first law, it is known that there exists a function $E(x)$ of the state x of the thermodynamic system that represents the stored energy. Consider the one-form

$$\beta := dE + PdV. \quad (S1)$$

The considerations in “Carnot and Caloric Theory” demonstrate that, in general, β is *not* an exact one-form (that is, there does not exist a state function Q , such that $\beta = dQ$). However, one can proceed as follows. Note that by the first law, β evaluated at a tangent vector equals the heat flow q . The curves on the state space whose tangent (velocity) vectors at every point of the curve are in the kernel of β are called *adiabatic curves*. Next, replace the formulation of the second law of thermodynamics by Kelvin, as given in “The Second Law of Thermodynamics” section with the following *alternative* statement: “Near any state x , there exist arbitrarily close states that cannot be joined to x by an adiabatic curve.” By Carathéodory’s theorem on one-forms [S1], it follows that there exist functions of the state called S (*entropy*) and τ , such that $\beta = \tau dS$. Equating τ with the absolute temperature T yields Gibbs’ fundamental relation, expressed by defining that the one-form

$$dE + PdV - TdS \quad (S2)$$

is zero on the state space. Note, however, the differences with the definition of entropy by Clausius (as revealed in “The Second Law of Thermodynamics” section): 1) The alternative formulation of the second law is different from the classical formulation of the second law, as expressed by Kelvin (or the equivalent formulation given by Clausius [20]); 2) the heat flow in the Born–Carathéodory approach to thermodynamics is a *derived* concept (in contrast with the theory of Clausius as well as cyclo-dissipativity theory); and 3) irreversible thermodynamics is not covered.

Another view on entropy in macroscopic thermodynamics was advocated by Callen [S2] and followed up on by many others [11]. In it, the second law of thermodynamics is replaced by the following *postulate* about the existence of the entropy as a function of the state and the *entropy maximum principle* [S2]:

There exists a function (called the entropy) of the extensive variables of any composite system, defined for all states and having the following property: the values assumed by the extensive variables in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained states.

A basic illustration of this postulate is a composite system consisting of two parts, with energies E_1 and E_2 that are constrained by the requirement that $E_1 + E_2$ is constant, together with the internal constraint that the wall between the two parts is nonconducting. The maximization of S over all E_1 and E_2 yields the values of E_1 and E_2 , which are obtained when the two parts are connected by a conducting wall.

In statistical mechanics (outside the realm of macroscopic thermodynamics), entropy was defined by Ludwig Boltzmann. His definition can be motivated, in a very rudimentary way, as follows. Obviously, $(d/dt)S \geq q/T$ implies that the entropy of a thermodynamic system without external heat flow can only increase. On the other hand (in accordance with statistical considerations), it is plausible that, from a *microscopic* perspective, the (very high-dimensional) state will converge to the state of *highest probability*. This led Boltzmann to establish his fundamental relationship $S = k \log \pi$, where π denotes the number of microscopic states corresponding to the macroscopic thermodynamic state, and k is the Boltzmann constant. Boltzmann’s definition of entropy inspired the definition of entropy in *information theory*, as given by Shannon. This provides another connection with systems and control theory. In general, control can be interpreted to entail two complementary aspects: 1) the shaping and routing of energy and 2) information gathering and processing. It is tempting to assume that thermodynamics may provide the key to *unify* both aspects.

Finally the work in [10] and its review [4] present a *middle-ground* theory of thermodynamics (that is, a foundational framework, which is in between macroscopic and statistical thermodynamics). It is based on deterministic large-scale dynamical systems theory and dissipativity theory and aimed at rigorously defining entropy and its related notions, making use of equipartition concepts.

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 [S2] H. Callen, *Thermodynamics*. New York: Wiley, 1960.

correctness, some of this terminology to a systems and control audience (see [7], [9], and [11] for a much extensive background). First, a *closed* thermodynamic system is a system that does not exchange matter but *can* exchange energy (through heat or work) with its surroundings. If it can exchange both energy and matter, it is called an *open* system. A closed thermodynamic system that also does not exchange energy is called an *isolated* system. Thus, a gas confined in a closed vessel whose volume is controlled by a piston is a *closed* system, while it is an *isolated* system if it is thermally isolated and the piston does not perform work on the surroundings. Note that this is different from the terminology in systems and control theory, where an isolated thermodynamic system is called a *closed* system and an *open* system if there is exchange with the surroundings (either by matter or energy flow).

Variables that are proportional to the amount of matter are called *extensive* variables, and their value for the overall system is the summation of their values for the parts into which the system is divided. Extensive variables thus scale with the size of the system. Examples of extensive variables are volume, energy, and mass. In contrast, *intensive* variables are not matter dependent in nature and do not depend on the total size of the system. Examples of intensive variables are temperature, pressure, and chemical potentials. One may draw analogies to electrical network theory. The charge in a capacitor could be called an extensive variable, while the voltage is an intensive variable. Similarly, the momentum of a point mass would be an extensive variable, while velocity is an intensive variable. There is also some relationship to the use of “through” and “across” variables in physical systems modeling. Across variables are similar to intensive variables, while the time integrals of through variables are extensive variables.

Although intensive variables such as temperature and pressure may spatially vary within the thermodynamic system, we will restrict our attention to thermodynamic systems, where the intensive variables are either spatially constant, or the spatial domain can be split into a finite number of parts on each of which the intensive variables are constant. The first situation is often referred to as a *homogeneous system* and the second as a *nonhomogeneous* (or composite) system consisting of a number of homogeneous parts. Whenever intensive variables vary with the spatial position, distributed-parameter (partial differential equations) models are required (which is outside the scope of the present article). A state of *equilibrium* is characterized by the temperature and other intensive variables being uniform throughout the system. If the temperature and other intensive variables are not uniform but are well defined locally, this is often referred to as *local equilibrium*. This terminology is confusing since a local equilibrium is *not* an equilibrium in the sense of dynamics. In fact, local equilibria give rise to *irreversible* (or *nonequilibrium*) thermodynamics.

Thermodynamic systems whose intensive variables are a single temperature T and pressure P will be referred to in this article as *simple thermodynamic systems*. A typical example is a

single-constituent gas in a container with volume V (an extensive variable of the system), where the variables V , P , and T are related through an equation $f(V, P, T) = 0$, called the *equation of state*. For example, an ideal gas satisfies the equation of state $PV = NRT$, with N being the number of moles of the gas and R representing the universal gas constant. The thermodynamic processes or transformations of a simple thermodynamic system are the conversion of one state [that is, a triple (V, P, T) satisfying the equation of the state] to another. Thermodynamic processes are the result of an interaction with the surroundings (for example, a piston changing the volume, or the absorption of heat from an external heat source). However, they may also be due to an internal *local* equilibrium (for example, two heat compartments with different temperatures connected by a conducting wall). A source of confusion in the exposition of thermodynamics is the use of terminology such as *quasi-reversible*, *infinitesimally slow*, or more recently, *horse-carrot transformations*. Remark 2 argues that such terminology can be avoided from a systems and control perspective.

Notation

The notations in this article are fairly standard. Given a function $H: \mathcal{X} \rightarrow \mathbb{R}$ for some n -dimensional manifold \mathcal{X} (for example, \mathbb{R}^n), denote by $(\partial H / \partial x)(x)$ the n -dimensional *column* vector of partial derivatives and by $(\partial H / \partial x^T)(x)$ the n -dimensional *row* vector of partial derivatives. Likewise, vectors v are column vectors, with v^T denoting its transpose (a row vector).

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics expresses two fundamental properties: 1) The different types of interaction of a thermodynamic system with its surroundings (for example, heat flow, mechanical work, or the flow of chemical species) all result in an exchange of a common quantity called *energy*. 2) There exists a function of the state of the thermodynamic system that represents the *internal energy* stored in the system, and the increase of this function during any time interval is the sum of the energies supplied to the system by the different forms of interaction with the surroundings during this time interval (*conservation of energy*). Thus, energy may manifest itself in different physical forms, which are *equivalent*, and to a certain extent, *exchangeable*. Note to a “certain extent” because a thermodynamic system cannot freely convert one form of energy into another. In fact, there are *restrictions* to this conversion expressed by the second law of thermodynamics, as discussed in “The Second Law of Thermodynamics” section.

Although the concept of energy may seem evident at this moment in the history of science, one should not underestimate the leap in abstraction that lies behind the formulation of the first law. Energy cannot be directly measured, unlike macroscopic thermodynamic quantities such as volume, pressure, and temperature. In particular, the

formulation of the equivalence of heat with other forms of energy took form rather late—around the middle of the 19th century—slowly replacing the caloric theory of heat fluid. For a brief historical perspective on the birth of the first law, see [7 Ch. 2] and “Carnot and Caloric Theory.”

How can the first law be expressed in a precise mathematical formulation using dissipativity theory? Consider a simple thermodynamic system described by volume V , pressure P , and temperature T . The mechanical power (rate of mechanical work) provided by the surroundings to the thermodynamic system is given by $-Pu_v$, where $u_v := \dot{V}$ is the rate of volume change. The usual sign convention in thermodynamics for the pressure P follows the physics convention, where Pu_v is the rate of mechanical work exerted by the system *on* the surroundings. Thus, the mechanical work done by the surroundings on the system during time interval $[t_1, t_2]$ is

$$-\int_{t_1}^{t_2} P(t)u_v(t)dt = -\int_{t_1}^{t_2} P(t)dV(t). \quad (1)$$

The second type of interaction with the surroundings is through *heat* delivered to the system by a *heat source*. Denote by q the heat flow (heat per second) from the heat source into the system. The *first law* is expressed by the existence of a function $E(x)$ of the thermodynamic state x [for example, (V, P, T) satisfying the equation of state], such that along all the possible trajectories of the thermodynamic system,

$$E(x(t_2)) - E(x(t_1)) = \int_{t_1}^{t_2} [q(t) - P(t)u_v(t)]dt \quad (2)$$

for all initial conditions $x(t_1)$ and all $t_1 \leq t_2$. That is, the increase of the total energy E of the thermodynamic system is equal to the incoming heat flow (through the *thermal*

port) minus the mechanical work performed by the system on its surroundings (through the *mechanical* port). Cyclo-dissipativity theory (as explained in “Cyclo-Dissipativity Theory”) immediately yields the right formalism to express the first law of thermodynamics. Namely, the first law amounts to the system being *cyclo-lossless* for the supply rate $s(q, P, u_v) = q - Pu_v$, with storage function E . Furthermore, in case E is bounded from below (and thus can be turned into a nonnegative storage function by adding a suitable constant), the thermodynamic system is *lossless*. Moreover, this could start from *external* cyclo-losslessness and then infer E as the unique (up to a constant) storage function. The formulation of the first law can be directly extended from simple thermodynamic systems to more involved ones; for example, if (apart from mechanical and thermal interaction with the surroundings) there is a mass inflow of chemical species, then the supply rate $q - Pu_v$ is extended to $q - Pu_v + \sum_k \mu_k v_k$. Here, $v_k = dN_k/dt$, with N_k being the mole number of the k th chemical species and μ_k representing its chemical potential [12].

By using energy as the *lingua franca* among different physical domains (such as mechanical, thermal, electrical, and chemical), the first law is at the heart of the modeling of complex multiphysics systems. The first law also emphasizes the role of multiphysics systems for *energy conversion*; energy from one physical domain can be converted into energy in another domain. Electrochemical devices (such as batteries) and electromechanical systems (such as electrical motors and generators) are among the many other examples whose origins already date back to the 19th century or earlier [7]. A second wave of research interest in multiphysics systems based on the exchange of energy was initiated around the middle of the 20th century, with

Carnot and Caloric Theory

Interestingly [7], [S3], Sadi Carnot started his investigations into the maximal efficiency of steam engines based on *caloric theory* (instead of the first law). The scientists before him, like Benjamin Franklin [S3], believed that heat flows through material by some (almost) weightless *caloric fluid* and that the amount of caloric fluid is *conserved*. In the same spirit, Carnot’s initial idea [S3] was that, just as water flows downhill, caloric fluid flows from hot to cold, and the steam engine utilizes this caloric flow to produce work (just as a water wheel takes energy from falling water). As a consequence, Carnot originally believed that in his Carnot cycle, the amount of heat Q_h absorbed from the hot reservoir is equal to the amount of heat $-Q_c$ released to the cold reservoir. It seems that he realized only later the fallacy of this idea [7]. By the time his work was made public (only in 1878; although Clapeyron used Carnot’s ideas in his description of the Carnot cycle in 1834, following Carnot’s death in 1832), the first law was already fully accepted (notably through the work of Joule and others; compare [7]).

From a mathematical perspective (without worrying about the physics), suppose that the caloric fluid *is* conserved and there exists a function Q of the state of the thermodynamic system (Q being the amount of caloric stored in the system), such that $(d/dt)Q = q$, where q is the caloric (heat) flow. Then, if additionally the first law $(d/dt)E = q - Pu_v$ holds, this would imply the existence of a third function W of the state, defined as $W := E - Q$ and satisfying $(d/dt)W = -Pu_v$. Said otherwise, the energy E would be the sum of two functions Q and W , which are storage functions for the supply rates q and $-Pu_v$, respectively. Typically, this can only be the case if the thermodynamic system consists of two *separate* parts: one for heat storage and one purely mechanical.

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an emphasis on the development of unified mathematical modeling and simulation languages for multiphysics systems. This led to the theory of port-based modeling, bond graphs [13]–[15], and eventually, port-Hamiltonian systems [16]–[19].

Even though the first law emphasizes the lossless conversion of one form of energy into another, it was realized from the very start of the development of thermodynamic theory that there are intrinsic *limitations* to this energy conversion. In particular, that heat *cannot* simply be converted into mechanical work. This is the origin of the *second law of thermodynamics*, directly motivated by the design of steam engines. While the first law prohibits the existence of a perpetual mobile of the first kind (energy cannot be created), the second law prohibits the existence of a perpetual mobile of the second kind (heat cannot be freely converted into mechanical work). This is the topic of the next section.

THE SECOND LAW OF THERMODYNAMICS

The cyclo-dissipativity interpretation of the second law of thermodynamics is much more involved than that of the first law. Note to begin with the formulation of the second law, as given by Lord Kelvin [20]:

A transformation of a thermodynamic system whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible.

As the work done by the thermodynamic system during time interval $[t_1, t_2]$ is equal to $\int_{t_1}^{t_2} P(t) dV(t) = \int_{t_1}^{t_2} P(t) u_V(t) dt$ (where $\dot{V} = u_V$ is the rate of volume change), Kelvin's formulation immediately implies that whenever the temperature is kept *constant*, any thermodynamic system is *cyclo-passive* with respect to the supply rate $-Pu_V$. Thus, for each constant temperature T at its thermal port, any thermodynamic system is cyclo-passive at its mechanical port. However, the second law is *stronger*. Namely, Kelvin's formulation also forbids the conversion into work of heat extracted from a source at constant temperature for all the transformations in which the system *also* interacts with a *second* heat source at a *different* temperature as long as the net heat taken from this second heat source is zero.

Carnot Cycle

The interaction with heat sources at different temperatures is crucial for the conversion of heat into mechanical work, as demonstrated by the famous *Carnot cycle* (due to Sadi Carnot, 1824). It can be described as follows. Consider a simple thermodynamic system (for example, a gas) with volume V , pressure P , and temperature T (interpreted as a *heat engine*). The system can be controlled in two ways: 1) via *isothermal* transformations, where *heat* is supplied to (or taken from) the system at a constant temperature (classically described as the interconnection of the thermodynamic system with an infinite heat reservoir at the temperature of the isothermal process); and 2) via *adiabatic* transformations, where the only

interaction with the surroundings is via *work* supplied to (or taken from) the system (classically described as the movement of a piston that changes the volume of the system, with a pressure equal to the pressure of the gas). Note that although during adiabatic transformations there is no heat absorbed or expelled (but only mechanical work is done), in isothermal transformations, the thermodynamic system is interacting with the surroundings *both* by heat and mechanical work (but in such a way that the temperature remains constant).

Consider a heat engine with *two* heat reservoirs: one at temperature T_h (hot) and the other at temperature T_c (cold), as in Figure 1. A *cycle* of the heat engine consists of two isothermal transformations and two adiabatic transformations. First, an isothermal transformation at temperature T_h taking the system from an initial state to another state. Second, an adiabatic transformation lowering the temperature of the system to T_c . Third, an isothermal transformation at temperature T_c taking the system to another state. Fourth, an adiabatic transformation that takes the system back to its original, initial state (see Figure 2). Denote the heat supplied to the system during the first isothermal transformation at temperature T_h by Q_h , and the heat supplied to the system during the other isothermal transformation at temperature T_c by Q_c (in case heat is released from the system, this means that Q_c is negative). Such a cycle will be denoted by (Q_h, T_h, Q_c, T_c) . For cycle (Q_h, T_h, Q_c, T_c) being a *Carnot cycle*, it is assumed

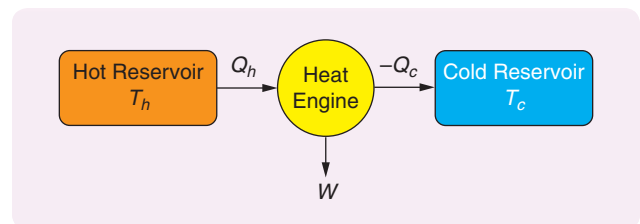


FIGURE 1 A heat engine with two heat reservoirs.

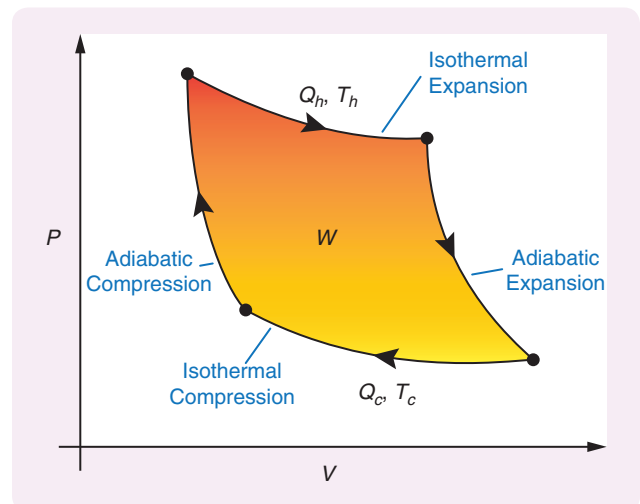


FIGURE 2 The Carnot cycle.

Cyclo-Dissipativity Theory

Dissipativity theory originates from the seminal work of Willems [6], continued by Hill and Moylan [32] and others; see [19] for an updated and extended exposition. The notion of dissipativity was relaxed to *cyclo-dissipativity* in [S4] and further explored in [S5], with recent extensions in [S6]. In the present context of thermodynamics, it is appropriate to emphasize *cyclo-dissipativity*. Consider a system with vector of state variables $x \in \mathcal{X}$ and vector of external variables $w \in \mathcal{W}$ (comprising the inputs u and outputs y). Furthermore, consider a *supply rate* $s: \mathcal{W} \rightarrow \mathbb{R}$.

Definition 14

A system is *cyclo-dissipative* (for supply rate s) if

$$\int_{t_1}^{t_2} s(w(t)) dt \geq 0 \quad (\text{S3})$$

for all $t_2 \geq t_1$ and all external trajectories $w(\cdot)$, such that $x(t_2) = x(t_1)$. In case (S3) holds with equality, the system is *cyclo-lossless*. Furthermore, the system is *cyclo-dissipative with respect to* x^* if (S3) holds for all $t_2 \geq t_1$ and all external trajectories $w(\cdot)$, such that $x(t_2) = x(t_1) = x^*$. Finally, it is *cyclo-lossless with respect to* x^* if this holds with equality.

Interpreting $s(w)$ as the “power” provided by the surroundings to the system, cyclo-dissipativity means that for any cyclic trajectory, the net amount of “energy” supplied to the system is nonnegative, and zero in the case of cyclo-losslessness. Hence, a cyclo-dissipative system cannot generate (but only dissipates) “energy” when returning to its initial state. In the special case of the supply rate $s(u, y) = y^T u$ (with the equally dimensioned vectors of inputs u and outputs y composing the vector of external variables w), “cyclo-dissipativity” is referred to as *cyclo-passivity*. Aside from the requirement that the state of the system follows a cyclic process, Definition 14 entails an *external* characterization of cyclo-dissipativity. To relate this external characterization to the internal-state dynamics, *dissipation (in)equality* and *storage function* are introduced.

Definition 15

Given a supply rate s , a function $F: \mathcal{X} \rightarrow \mathbb{R}$ is called a *storage function* if it satisfies the *dissipation inequality*

$$F(x(t_2)) - F(x(t_1)) \leq \int_{t_1}^{t_2} s(w(t)) dt \quad (\text{S4})$$

for all $t_2 \geq t_1$, all initial conditions $x(t_1)$, and all external trajectories $w(\cdot)$ where $x(t_2)$ is the state at time t_2 corresponding to initial condition $x(t_1)$ and external trajectory $w(\cdot)$. Equation (S4) with equality is called the *dissipation equality*.

Interpreting as before $s(w(t))$ as “power” supplied to the system at time t , and $F(x(t))$ as stored “energy” while the system is at state $x(t)$, the existence of a storage function means that an increase of the stored energy can only occur due to

externally supplied power. The following theorem [S6] extends the results in [S5] and shows the equivalence between the external characterization of cyclo-dissipativity and cyclo-losslessness and the existence of storage functions.

Theorem 16

Consider a system with supply rate s . If there exists a storage function $F: \mathcal{X} \rightarrow \mathbb{R}$, then the system is cyclo-dissipative. It is cyclo-lossless if F satisfies (S4) with equality. Assume that the system is reachable from some ground-state x^* and controllable to this same state x^* . (It is immediate that this property is independent of the choice of x^* .) Define the (possibly extended) functions $F_{ac}: \mathcal{X} \rightarrow \mathbb{R} \cup \infty$ and $F_{rc}: \mathcal{X} \rightarrow -\infty \cup \mathbb{R}$ as

$$\begin{aligned} F_{ac}(x) &= \sup_{\substack{w, \mathcal{T} \geq 0 \\ x(0)=x, x(\mathcal{T})=x^*}} - \int_0^{\mathcal{T}} s(w(t)) dt, \\ F_{rc}(x) &= \inf_{\substack{w, \mathcal{T} \geq 0 \\ x(-\mathcal{T})=x^*, x(0)=x}} \int_{-\mathcal{T}}^0 s(w(t)) dt, \end{aligned} \quad (\text{S5})$$

where the supremum and infimum are taken over all external trajectories $w(\cdot)$ and $\mathcal{T} \geq 0$, satisfying $x(0) = x, x(\mathcal{T}) = x^*$ and (respectively) $x(-\mathcal{T}) = x^*, x(0) = x$. Then, the system is cyclo-dissipative with respect to x^* if and only if

$$F_{ac}(x) \leq F_{rc}(x), \text{ for all } x \in \mathcal{X}. \quad (\text{S6})$$

Furthermore, if the system is cyclo-dissipative with respect to x^* , then $F_{ac}: \mathcal{X} \rightarrow \mathbb{R}$ and $F_{rc}: \mathcal{X} \rightarrow \mathbb{R}$, and they define the storage functions (implying the system is cyclo-dissipative). Furthermore, $F_{ac}(x^*) = F_{rc}(x^*) = 0$ while any other storage function F satisfies

$$F_{ac}(x) \leq F(x) - F(x^*) \leq F_{rc}(x).$$

If the system is cyclo-lossless with respect to x^* , then $F_{ac}(x) = F_{rc}(x), x \in \mathcal{X}$ [implying uniqueness (up to a constant) of the storage function].

Note that the first statement of this theorem (the existence of a storage function implies cyclo-dissipativity) is obvious: Simply substitute $x(t_1) = x(t_2)$ into (S4). For the proof of the rest of this theorem, refer to [S6].

Apart from the cyclo-lossless case, the storage functions of dissipative systems are far from unique. The following proposition from [S6] ensures uniqueness by imposing a *weakened* form of cyclo-losslessness.

Proposition 17

Suppose that the system is reachable from and controllable to x^* and cyclo-dissipative with respect to x^* . Assume additionally that for every x , there exists a solution $(x_i(\cdot), w_i(\cdot))$ on some time interval $[0, \mathcal{T}_i]$, such that $x_i(0) = x_i(\mathcal{T}_i) = x^*$ and $x_i(\tau) = x$ for some $\tau \in [0, \mathcal{T}_i]$ satisfying

$$\int_0^{\mathcal{T}_1} s(w_I(t)) dt = 0. \quad (S7)$$

Then, $F_{ac}(x) = F_{rc}(x)$ for all $x \in \mathcal{X}$, and the storage function is unique up to a constant and given by

$$F(x) = \int_0^{\tau} s(w_I(t)) dt = - \int_{\tau}^{\mathcal{T}_1} s(w_I(t)) dt, \quad (S8)$$

where $x_I(\tau) = x$ and $x_I(0) = x_I(\mathcal{T}_1) = x^*$.

Note that (S7) means that the system is *weakly* cyclo-lossless with respect to x^* , in the sense that for every x there exists *at least one* cyclic trajectory passing through x and x^* satisfying (S3) with *equality*. The other cyclic trajectories passing through x and x^* may satisfy (S3) only with *inequality*.

Remark 18

With little effort, Proposition 17 (as proved in [S6]) can be generalized as follows. Suppose that the system is reachable from and controllable to x^* . Then, the system is cyclo-dissipative with respect to x^* with a unique (up to a constant) storage function if and only if for every x ,

$$\inf \int_{t_1}^{t_2} s(w(t)) dt = 0, \quad (S9)$$

where the infimum is taken over all trajectories through x with $x(t_1) = x(t_2) = x^*$.

The stronger notion of dissipativity [6], historically introduced *before* the notion of cyclo-dissipativity, *starts* from the dissipation inequality (S4) and is restricted to *nonnegative* storage functions. See [S7] for further information.

Definition 19

A system is *dissipative* (for the supply rate s) if there exists a *nonnegative* storage function F . As the addition of an arbitrary constant to a storage function again leads to a storage function, the requirement of nonnegativity of F can be relaxed to F being *bounded from below*. Furthermore, the system is *lossless* if there exists a nonnegative storage function F satisfying the dissipation inequality (S4) with *equality*.

Nonnegative storage functions are candidate Lyapunov functions for the internal-state dynamics for $s(w) = 0$ [6], [19], [32]. In this way, dissipativity theory connects the external stability properties of the system to internal Lyapunov stability properties. An *external* characterization of dissipativity is obtained as follows [6].

Theorem 20

The system is dissipative (for the supply rate s) if and only if

$$F_a(x) := \sup_{w, \mathcal{T} \geq 0} - \int_0^{\mathcal{T}} s(w(t)) dt < \infty \quad (S10)$$

for every x , where the supremum is taken over all external trajectories $w(\cdot)$ of the system corresponding to initial condition $x(0) = x$ and all $\mathcal{T} \geq 0$. Obviously, $F_a(x) \geq 0$. Furthermore, if

$F_a(x) < \infty$ for every x , then F_a is a nonnegative storage function and is the *minimal* nonnegative storage function. Additionally, if the system is reachable from some ground-state x^* , then it is dissipative if and only if $F_a(x^*) < \infty$.

Interpreting again $s(w)$ as the “power” supplied to the system, $F_a(x)$ is the *maximal “energy”* that can be extracted from the system at initial condition x . Thus, Theorem 20 states that the system is dissipative if and only if from any initial state x , only a *finite* amount of “energy” can be extracted. This should be contrasted with the external characterization (S3) of cyclo-dissipativity, stating that the system is cyclo-dissipative if and only if the net “energy” supplied to the system along any cyclic trajectory is greater than or equal to zero. In the case where the system is a cyclo-dissipative system, it may still be possible to extract an *infinite* amount of “energy” (namely, if the storage function is not bounded from below). The storage functions not bounded from below are not uncommon in physical systems modeling; for example, the gravitational energy between two masses is proportional to $-1/r$, with $r \geq 0$ being the distance between the two masses (and is thus *not* bounded from below).

Remark 21

For reachable linear systems with quadratic supply rates, dissipativity is often equivalent to $F_a(0) = 0$, yielding the familiar external characterization $\int_0^{\mathcal{T}} s(w(t)) dt \geq 0$ for all the trajectories starting from $x(0) = 0$ [19].

Finally, by assuming *differentiability* of the storage function, the dissipation inequality can be replaced by an (easier) differential version. Consider the input-state-output system

$$\begin{aligned} \dot{x} &= f(x, u), \\ y &= h(x, u), \end{aligned} \quad (S11)$$

with state $x \in \mathcal{X}$ and vector of external variables $w = (u, y)$, where u is the vector of inputs and y the vector of outputs. Consider a supply rate $s(u, y)$. The differentiable function $F: \mathcal{X} \rightarrow \mathbb{R}$ satisfies the dissipation inequality (S4) (and thus is a storage function) if and only if it satisfies the *differential dissipation inequality* [6], [19], [32]

$$\frac{\partial F}{\partial x}(x) f(x, u) \leq s(u, h(x, u)), \quad \text{for all } x, u. \quad (S12)$$

It satisfies the dissipation *equality* if (S12) holds with equality.

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that $(-Q_c, T_c; -Q_h, T_h)$ is a feasible cycle as well. Thus, a Carnot cycle can be *reversed*, leading to the same initial state. This is referred to as a *reversibility*, although it is often understood in a stronger sense: The path in the state space of the thermodynamic system resulting from applying the four transformations can also be followed in the reverse direction [9]. In the present relaxed definition of reversibility, it is only required that the amounts of heat supplied or released are the negative of those of the original cycle. This is called *heat supply reversibility* and is summarized as follows.

Definition 1

Consider a simple thermodynamic system. A *cycle* $(Q_h, T_h; Q_c, T_c)$ is the sequence of an isothermal (with temperature T_h and supplied heat Q_h), adiabatic, isothermal (with temperature T_c and supplied heat Q_c), and a final adiabatic transformation (which returns the system to its initial state). It is called a *Carnot cycle* if there also exists a cycle $(-Q_c, T_c; -Q_h, T_h)$.

Remark 2

Unfortunately, the exposition of the Carnot cycle is often obscured by the use of terminologies such as “infinitesimally slow,” “quasi-reversible,” and “such that the system remains at equilibrium.” This is largely due to a scientific tradition that thinks about the interaction of the system with its surroundings in a different way than in systems and control. For example, an isothermal transformation is regarded as the result of the “real” physical action of a force exerted by a piston on the gas (implying that the pressure delivered by the piston could be different from the pressure of the gas). Furthermore, during the time when the system is actuated by the piston, it is in “real” physical contact with a heat reservoir at a certain temperature (and thus the temperature of the heat reservoir could differ from that of the gas). In contrast, within systems and control (or, for example, electrical network theory), it has become common use to the concept of an “ideal” control action, where the pressure and temperature are directly controlled. This idealized systems and control perspective is very appropriate for the description of the Carnot cycle. There is a good reason for this; the fundamental problem of Carnot was to give an answer to the *control* problem of optimal conversion of heat into work.

A crucial step in the deduction of the consequences of the second law is to show that for Carnot cycles $(Q_h, T_h; Q_c, T_c)$, the quantity

$$\frac{Q_h}{-Q_c} \quad (3)$$

depends only on the temperatures T_h and T_c . This will lead to the celebrated Clausius (in)equality, and ultimately, the definition of entropy. The following indicates the main line

of reasoning, based on the elegant exposition (in a slightly different setting) in [20]. First note the following observation, based on an additional (but very reasonable) assumption: *If we bring two heat reservoirs with temperatures $T_h > T_c$ into contact, then any positive amount of heat can be disposed from the reservoir with temperature T_h to that with temperature T_c .* Consider now a cycle $(Q_h, T_h; Q_c, T_c)$ from a given initial state. Assume that the mechanical work $W := \oint P(t) dV(t)$ done by the thermodynamic system on the surroundings during this cycle is *positive* (that is, $W > 0$). Then, by invoking the aforementioned assumption, any cycle $(Q_h, T_h; Q_c, T_c)$ with $T_h > T_c$ is such that $Q_h > 0$, $Q_c < 0$ (that is, the thermodynamic system absorbs heat during the isothermal transformation corresponding to the high temperature T_h , and it expels heat during the isothermal transformation corresponding to the low temperature T_c). Assume, on the contrary, that $Q_c \geq 0$. Complement cycle $(Q_h, T_h; Q_c, T_c)$ with the flow of an amount of heat from the hot (T_h) to the cold (T_c) reservoir, which is equal to $-Q_c$. Then, the net amount of heat absorbed by the cold reservoir is zero, and thus, by Kelvin’s formulation of the second law, the mechanical work W satisfies $W \leq 0$ (yielding a contradiction). Thus, necessarily, $Q_c < 0$. Furthermore, by the first law, $W = Q_c + Q_h$. Hence, as $W > 0$ and $Q_c < 0$, it follows that $Q_h > 0$ (as claimed).

Remark 3

Consequently, for a Carnot cycle $(Q_h, T_h; Q_c, T_c)$ with $W > 0$, the reversed cycle $(-Q_c, T_c; -Q_h, T_h)$ satisfies $-Q_c > 0$, $-Q_h < 0$. Furthermore, the work done by the system on the surroundings during this reversed cycle equals $-Q_c - Q_h = -W < 0$. This corresponds to a *refrigerator* or *heat pump*, where mechanical work is done on the system to transfer heat from the cold heat reservoir to the hot heat reservoir.

Now, to show that the quantity in (3) depends only on T_h and T_c , let $(Q_h, T_h; Q_c, T_c)$ be a Carnot cycle. Consider another cycle $(Q'_h, T_h; Q'_c, T_c)$ (from the same initial state); also with $Q'_h > 0$, $Q'_c < 0$. First assume that the fraction Q_h/Q'_h is a nonnegative rational number, that is,

$$\frac{Q_h}{Q'_h} = \frac{N'}{N} \quad (4)$$

for some nonnegative integers N , N' . Consider the total transformation consisting of N cycles $(-Q_c, T_c; -Q_h, T_h)$ and N' cycles $(Q'_h, T_h; Q'_c, T_c)$. Then the total amount of heat absorbed from the hot reservoir T_h is, by construction, zero. Therefore, by Kelvin’s formulation of the second law, the total work W done by the system satisfies $W \leq 0$. Alternately by the first law, $W = N(-Q_c) + N'Q'_c$ (and thus, $N'Q'_c \leq NQ_c$). Together with (4), this yields

$$\frac{Q_h}{-Q_c} \geq \frac{Q'_h}{-Q'_c}. \quad (5)$$

As any real number Q_h/Q'_h can be approximated arbitrarily well by a rational number, the inequality (5) holds for *any* Carnot cycle $(Q_h, T_h; Q_c, T_c)$ and any other cycle $(Q'_h, T_h; Q'_c, T_c)$ from the same initial state with $Q'_h > 0$, $Q'_c < 0$. Furthermore, if $(Q_h, T_h; Q'_c, T_c)$ is a Carnot cycle as well, then by exchanging the two Carnot cycles in the aforementioned reasoning, the opposite inequality is obtained, thus proving

$$\frac{Q_h}{-Q_c} = \frac{Q'_h}{-Q'_c}. \quad (6)$$

Hence, the fraction $Q_h/-Q_c$ is the same for all Carnot cycles between the temperatures T_c , and T_h , and thus,

$$\frac{Q_h}{-Q_c} = f(T_c, T_h) \quad (7)$$

for some function f . Involving a third, arbitrary temperature T_0 and heat Q_0 , the aforementioned arguments can be repeated, yielding

$$\frac{Q_c}{-Q_0} = f(T_0, T_c), \quad \frac{Q_h}{-Q_0} = f(T_0, T_h). \quad (8)$$

Defining $\tau(T) := f(T_0, T)$, this implies

$$\frac{Q_h}{-Q_c} = \frac{\tau(T_h)}{\tau(T_c)}. \quad (9)$$

The function $\tau(T)$ amounts to a *rescaling* of the temperatures (in fact, it corresponds to the absolute thermodynamic scale of temperature [8], [20]). For convenience, the same notation T is used for the rescaled temperature $\tau(T)$. Thus, for any Carnot cycle $(Q_h, T_h; Q_c, T_c)$,

$$\frac{Q_h}{-Q_c} = \frac{T_h}{T_c} \quad (10)$$

or equivalently,

$$\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0. \quad (11)$$

Furthermore, in view of (5) and (11), an arbitrary (not necessarily Carnot) cycle $(Q_h, T_h; Q'_c, T_c)$ satisfies

$$\frac{Q'_h}{T_h} + \frac{Q'_c}{T_c} \leq 0. \quad (12)$$

Remark 4

The second law is a statement about *all* thermodynamic systems; not just a particular system (as is the norm in systems and control). This allows for consideration of thermodynamic processes consisting of a cycle of one system and a reversed Carnot cycle of a second one. In particular, this *universality* implies that the rescaling of the temperature holds for all thermodynamic systems in the same way, leading to a uniform absolute temperature.

Maximal Efficiency of the Carnot Cycle

The *efficiency* of a cycle is defined as the performed mechanical work divided by the absorbed heat at high temperature, given as

$$\frac{W}{Q_h} = \frac{Q_h + Q_c}{Q_h} = 1 - \frac{-Q_c}{Q_h}. \quad (13)$$

It follows from (5) that Carnot cycles enjoy *maximal efficiency* among all cycles, and by (6), this efficiency is independent of which Carnot cycle is taken (and as described Remark 4, independent of the system considered). Furthermore by (11), the efficiency of a Carnot cycle is equivalently given as

$$1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h}. \quad (14)$$

In particular, this means that to increase efficiency, it is most advantageous to lower T_c . On the other hand, in many applications (such as the classical the steam engine), T_c is just the temperature of the environment (which *cannot* be controlled). The “Kelvin and the Limits to Energy Conversion” section addresses the control problems suggested by the second law and the Carnot cycle in the general context of energy conversion.

Clausius’ Inequality

The fundamental equality (11) for a Carnot cycle $(Q_h, T_h; Q_c, T_c)$ and the inequality (12) for an arbitrary cycle $(Q'_h, T_h; Q'_c, T_c)$ can be generalized as follows (see [20] for more details). Consider a *complex* cycle $(Q_1, T_1; \dots; Q_n, T_n)$ consisting of n isothermals at temperatures T_i and absorbed heat quantities Q_i , $i = 1, 2, \dots, n$, and interlaced by n adiabatics. Such a complex cycle $(Q_1, T_1; \dots; Q_n, T_n)$ is called *heat-supply reversible* if $(-Q_n, T_n; \dots; -Q_1, T_1)$ is also a feasible cycle (returning to the same state). Now consider an auxiliary heat source with temperature T_0 and n Carnot cycles $(Q_i, T_i; Q_{i,0}, T_0)$ operating between the temperatures T_i $i = 1, \dots, n$ and T_0 . According to (11),

$$-Q_{i,0} = \frac{T_0}{T_i} Q_i. \quad (15)$$

Consider the total transformation consisting of the complex cycle $(Q_1, T_1; \dots, Q_n, T_n)$, together with the heat supply reversed Carnot cycles $(-Q_{i,0}, T_0; -Q_i, T_i)$, $i = 1, \dots, n$. The net exchange of heat with each of the sources with temperatures T_1, \dots, T_n is zero, while the auxiliary source at temperature T_0 , in view of (15), absorbs a total heat

$$\sum_{i=1}^n -Q_{i,0} = T_0 \sum_{i=1}^n \frac{Q_i}{T_i}. \quad (16)$$

By Kelvin’s formulation of the second law, this quantity should be less than or equal to zero, or equivalently,

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0. \quad (17)$$

Furthermore, if the complex cycle $(Q_1, T_1; \dots; Q_n, T_n)$ is heat-supply reversible, then the opposite inequality is analogously proven, thus yielding

$$\sum_{i=1}^n \frac{Q_i}{T_i} = 0. \quad (18)$$

A slight extension [approximating continuous heat flow time-functions $q(\cdot)$ by step functions with step values Q_1, \dots, Q_n] then yields the celebrated *Clausius inequality*

$$\oint \frac{q(t)}{T(t)} dt \leq 0 \quad (19)$$

for all cyclic processes $(q(\cdot), T(\cdot))$, and

$$\oint \frac{q(t)}{T(t)} dt = 0 \quad (20)$$

for heat-supply reversible cyclic processes.

FROM CLAUSIUS' INEQUALITY TO ENTROPY

From the perspective of cyclo-dissipativity theory (see "Cyclo-Dissipativity Theory"), the Clausius inequality (19) is exactly the same as the *cyclo-dissipativity* of any thermodynamic system with respect to the supply rate $-(q/T)$ (where q is the heat flow into the thermodynamic system, and T is the temperature). Thus, assuming reachability from and controllability to some ground-state x^* , this means that there exists a *storage function* F of the state, such that $F(x(t_2)) \leq F(x(t_1)) + \int_{t_1}^{t_2} -(q(t)/T(t)) dt$ (see Theorem 16 in "Cyclo-Dissipativity Theory"). Equivalently, the function $S := -F$ satisfies

$$S(x(t_2)) - S(x(t_1)) \geq \int_{t_1}^{t_2} \frac{q(t)}{T(t)} dt, \quad (21)$$

and its differential version (assuming S to be differentiable) is

$$\frac{d}{dt} S \geq \frac{q}{T}. \quad (22)$$

The function S was called *entropy* by Clausius, from the Greek word $\tau\rho\omicron\pi\eta$ for "transformation." The dissipativity formulation (21) of the second law already appears in [6] (see also [10] and [21]); however, it is assumed that F is bounded from below (and thus, S is bounded from above), corresponding to dissipativity instead of cyclo-dissipativity. Physically, there is generally no reason why the entropy S should be bounded from above.

From the perspective of (cyclo-)dissipativity theory, the storage function F need not be unique. To guarantee the uniqueness of F , and therefore of the entropy S (which is very desirable from a physics perspective), Proposition 17 in "Cyclo-Dissipativity Theory" may be exploited. Once it is assumed that (given some ground-state) for every thermodynamic state, there exists a cyclic transformation through this state and the ground-state satisfying

$$\oint \frac{q(t)}{T(t)} dt = 0, \quad (23)$$

then by Proposition 17, entropy S is unique (up to a constant). The uniqueness of S is (explicitly or implicitly) always assumed in the expositions of classical thermodynamics. Cyclo-dissipativity theory thus provides a solid basis for this assumption.

According to [7], Clausius interpreted the term q/T as the part of the infinitesimal transformation $(d/dt)S$, which is *compensated* by the opposite rate of change $-(q/T)$ of the entropy of the surroundings; that is, of the heat reservoir supplying the heat to the thermodynamic system. The remaining part,

$$\sigma := \frac{d}{dt} S - \frac{q}{T} \geq 0, \quad (24)$$

was called the *uncompensated transformation* by Clausius ("unkompensierte Verwandlung" in German) [7]. Thus, the second law implies that the uncompensated transformation is always nonnegative. The quantity $\sigma \geq 0$ is also called the *irreversible entropy production*, and it is the starting point for a broader discussion of irreversible thermodynamics in the "Irreversible Thermodynamics" section. Note that if σ is nonzero, then $\oint (q(t)/T) dt < 0$ along any cyclic path with *constant* temperature T . Hence, the thermodynamic system expels a positive amount of heat to its surroundings due to an irreversible conversion of (for example, mechanical) energy into heat.

Remark 5

It follows from Theorem 20 in "Cyclo-Dissipativity Theory" that the thermodynamic system is *dissipative* instead of being just cyclo-dissipative (with respect to the supply rate $-(q/T)$) if and only if for all states x ,

$$F_a(x) = \sup \int \frac{q(t)}{T(t)} dt < \infty, \quad (25)$$

where the supremum is taken over all heat flow functions $q(\cdot)$ and corresponding temperature profiles $T(\cdot)$ resulting from $x(0) = x$. Furthermore, if (25) holds, then $-F_a$ is *maximal* among all the *nonpositive* functions satisfying (21). See [21] for an investigation of the existence of a *nonnegative* storage function based on a combination of the energy and entropy functions.

Back to the Carnot Cycle

The introduction of the entropy S sheds new light on the Carnot cycle [8], [9]. Indeed, the closed curve in the (V, P) diagram consisting of two isothermals interlaced with two adiabatics corresponds in the (S, T) diagram to a very simple rectangular curve (see Figure 3), where $S_2 - S_1 = Q_h/T_h = -Q_c/T_c$. Furthermore, the resulting map from the (S, T) to the (V, P) diagram is *area-preserving*: The area within the rectangular closed curve in the (S, T) diagram (the net amount of absorbed

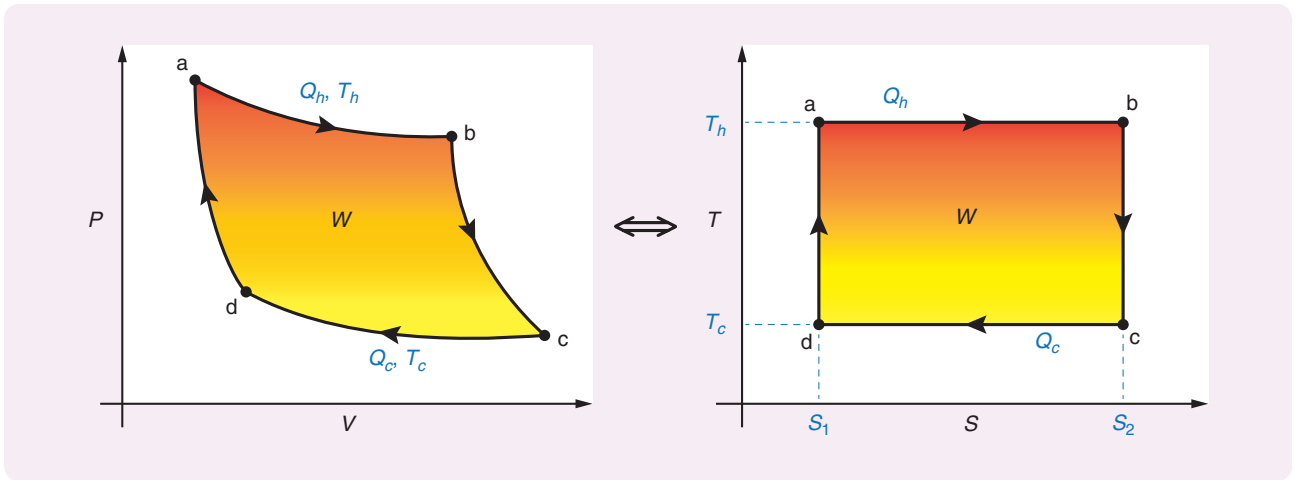


FIGURE 3 The Carnot cycle in the (V, P) and (S, T) diagrams.

heat $Q_h + Q_c$ is, by the first law, equal to the area in the (V, P) diagram circumscribed by the Carnot cycle (the amount of work W done by the system on the surroundings).

The discussion of the Carnot cycle ($Q_h, T_h; Q_c, T_c$) is closed with an intriguing reinterpretation of the fundamental equality (11). See [22] for an account of similar reasoning in the original work of Clausius. Rewrite (11) as

$$0 = \frac{Q_h}{T_h} + \frac{Q_c}{T_c} = \frac{Q_h + Q_c}{T_h} + Q_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right), \quad (26)$$

or equivalently,

$$\frac{Q_h + Q_c}{T_h} = -Q_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right). \quad (27)$$

Note that $-Q_c$ is the net amount of heat flowing from the hot heat source to the cold one, while $(1/T_c) - (1/T_h)$ is known as the *thermodynamic force* between the two heat sources (see the “Irreversible Thermodynamics” section). Furthermore, $Q_h + Q_c$ is the total heat supplied by the two sources to the thermodynamic system (which, by the first law, equals the work W performed by the system on its surroundings) and corresponds to the left part of the upper isothermal in the Carnot cycle in Figure 4. Hence, (27) means that the entropy increase $(Q_h + Q_c)/T_h$ due to the supplied heat during the left part of the upper isothermal is equal to the change in entropy due to a direct heat flow $-Q_c$ from hot to cold (the falling caloric flow in the original interpretation of Carnot; see “Carnot and Caloric Theory”).

Finally, there exist other interesting cycles aside from the aforementioned ones, consisting of isothermals and adiabatics. Like the Carnot cycle originates from the steam engine, most of these alternative cycles derive from the operation of other types of engines. For example, the Otto cycle is described in the (V, P) diagram by two adiabatics and two isochores (constant volume), the Diesel cycle by two isobars (constant pressure) and two adiabatics, and the Stirling cycle by two isothermals and two isochores. An

extensive discussion of them is given in [9]. The use of such cycles for energy conversion and harvesting poses several interesting control problems (see also the next section).

Kelvin and the Limits to Energy Conversion

It was previously noted that Kelvin’s formulation of the second law implies that the thermodynamic system (when kept at constant temperature T) is *cyclo-passive* with respect to the supply rate $-Pu_v$ corresponding to mechanical work. By the main theorem of cyclo-dissipativity (see the Theorem 16 in “Cyclo-Dissipativity Theory”), this means that for each constant temperature T , there exists a function F_T of the state x of the thermodynamic system satisfying

$$F_T(x(t_2)) - F_T(x(t_1)) \leq \int_{t_1}^{t_2} -P(t)u_v(t)dt. \quad (28)$$

This expresses the property that no thermodynamic system can convert thermal energy from a heat source at a constant temperature into mechanical work while returning to its original state. From a general system-theoretic perspective, this leads to the following question. Consider

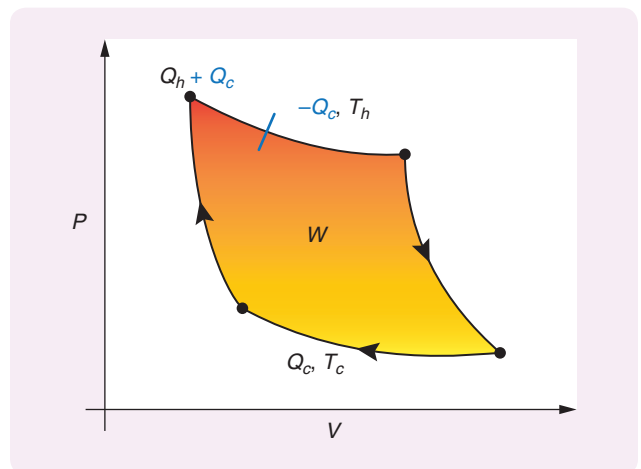


FIGURE 4 The Carnot cycle reinterpreted.

a system (as in Figure 5) with two ports, denoted as (u_1, y_1) and (u_2, y_2) , which is cyclo-passive with respect to the supply rate $s(u_1, u_2, y_1, y_2) = y_1^\top u_1 + y_2^\top u_2$. That is, there exists a state function F such that

$$\frac{d}{dt}F \leq y_1^\top u_1 + y_2^\top u_2. \quad (29)$$

Under which conditions is it *not* possible to transform energy at port 1 into energy at port 2 while keeping y_1 constant? Stated differently, what is so special about thermodynamic systems, and are there any systems other than thermodynamic systems that *cannot* transform energy from one port into the other while keeping the output at the first port (temperature T in the thermodynamic case) constant? The answer to this question is yes, there are quite a few other systems sharing this property of limits to energy conversion. In fact, sufficient (and often necessary) conditions on the system for this to happen are discussed in [23], together with several examples from different areas (for example, synchronous machines, dc machines, and capacitor microphones). Conversely, for such systems, this directly motivates the consideration of cycles (classical or generalized) that *do* convert energy from one port into the other. Similar to cycles in the thermodynamic realm, this leads to (open) questions of *maximal efficiency* of energy conversion. Returning to the original dissipation inequality (28), note that even if the storage function F_T for each T is unique, it is so only *up to a constant*, which may arbitrarily depend on T . This is intimately related to the fact that Kelvin's formulation of the second law is *stronger* than just cyclo-passivity for every T . The right choice of F_T for every T is provided by the *Helmholtz free energy*; one of the thermodynamic potentials that is discussed in the "Gibbs and the Thermodynamic Phase Space" section.

IRREVERSIBLE THERMODYNAMICS

Recall the dissipation inequality $(d/dt)S \geq (q/T)$, equivalently rewritten as

$$\frac{d}{dt}S = \frac{q}{T} + \sigma, \quad \sigma \geq 0, \quad (30)$$

where $\sigma := (d/dt)S - (q/T)$ is the *irreversible entropy production* [7] ("uncompensated transformation," in the terminology of Clausius). Irreversible thermodynamics is concerned with the dynamics of thermodynamic systems in case σ is

different from zero, implying an autonomous (independent from external heat flow) increase of the entropy S . Sometimes it is also referred to as *nonequilibrium thermodynamics* because it results from (internal) nonequilibrium conditions. Perhaps the simplest example of irreversible dynamics and irreversible entropy production is offered by the *heat exchanger*. Consider two heat compartments, with temperatures T_h and T_c ("hot" and "cold"), connected by a heat-conducting wall. In the absence of the conducting wall, these are two separate systems with entropies S_h and S_c , satisfying

$$\frac{d}{dt}S_h = \frac{q_h}{T_h}, \quad \frac{d}{dt}S_c = \frac{q_c}{T_c}. \quad (31)$$

Due to the conducting wall, there is a heat flow q from the hot to the cold compartment, which (in view of the first law) is such that $q = -q_h = q_c$. Hence, the total entropy $S := S_h + S_c$ satisfies

$$\frac{d}{dt}S = -\frac{q}{T_h} + \frac{q}{T_c} = \left(\frac{1}{T_c} - \frac{1}{T_h}\right)q, \quad (32)$$

where (using Fourier's law for heat conduction) $q = \lambda(T_h - T_c)$ for some positive constant λ . This yields the following expression for the irreversible entropy production $\sigma = (d/dt)S$ (note that there is no external heat flow):

$$\sigma = \left(\frac{1}{T_c} - \frac{1}{T_h}\right)\lambda(T_h - T_c) = \lambda \frac{(T_h - T_c)^2}{T_h T_c} \geq 0. \quad (33)$$

A second simple example refers to the adiabatics in the classical Carnot cycle of a gas in a volume controlled by a piston. If the pressure P of the gas is not considered to be the direct control variable (but instead, one distinguishes between a pressure P_{piston} on the piston and a pressure P_{gas} of the gas), then, during the expansion phase leading to the irreversible entropy production, σ is given by

$$\sigma = \frac{P_{\text{gas}} - P_{\text{piston}}}{T} J, \quad (34)$$

where J is the rate of volume change. Typically, J will be positively proportional to the difference $P_{\text{gas}} - P_{\text{piston}}$, implying that $\sigma \geq 0$.

Chemical Reaction Networks

A more involved example of irreversible thermodynamics is the dynamics of (nonisothermal) *chemical reaction networks* (see [7] for further thermodynamic background). Consider for simplicity an *isolated* chemical reaction network (no incoming or outgoing mass flow and no external heat flow), with m chemical species and r reactions. Disregard volume and pressure and model the state of the chemical reaction network accordingly by the vector $x \in \mathbb{R}^m$ of concentrations of the chemical species. Then the dynamics takes the form

$$\dot{x} = Nv(x), \quad (35)$$

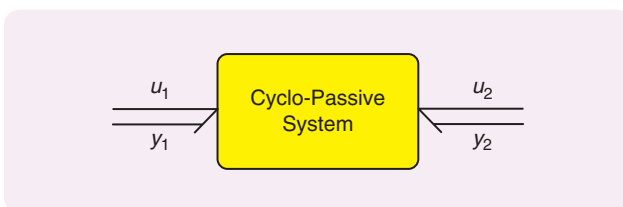


FIGURE 5 A two-port cyclo-passive system.

where N is an $m \times r$ matrix (called the *stoichiometric matrix*), and $v \in \mathbb{R}^r$ is the vector of reaction fluxes. The stoichiometric matrix N , which consists of positive and negative integer elements, captures the basic conservation laws of the reactions. Chemical reaction network theory, originating from [24]–[26], identifies the edges of the underlying directed graph with the *chemical reactions* and the nodes with the *complexes* of the chemical reactions (that is, all the different left- and right-hand sides of the reactions in the network). This means [27], [28] that the stoichiometric matrix N is factorized as $N = ZB$, with B denoting the $c \times r$ *incidence matrix* of the graph of complexes, and Z being the $m \times c$ *complex composition matrix* (a matrix of nonnegative integers) whose ρ th column captures the expression of the ρ th complex in the m chemical species. It is shown in [27] that the dynamics $\dot{x} = Nv(x)$ of a large class of chemical reaction networks (including detailed-balanced mass-action kinetics networks) can be written as

$$\dot{x} = -Z\mathbb{L} \text{Exp}\left(\frac{1}{RT}Z^\top\mu(x)\right), \quad (36)$$

where $\text{Exp}: \mathbb{R}^c \rightarrow \mathbb{R}^c$ is the vector exponential mapping $\text{Exp}(z) = (\exp z_1, \dots, \exp z_c)^\top$, R is the gas constant, T is the temperature, and μ is the m -dimensional vector of *chemical potentials* of the chemical species (for which, in the case of detailed-balanced mass-action kinetics, an explicit expression is available). Furthermore, the matrix $\mathbb{L} := BKB^\top$ in (36) defines a *weighted Laplacian* matrix for the graph of complexes, with the diagonal elements of the diagonal matrix K given by the so-called conductances $\kappa_1, \dots, \kappa_r$ (which are dependent on temperature T and the reference state). This leads to the following fundamental property [27]:

$$\gamma^\top \mathbb{L} \text{Exp} \gamma \geq 0 \text{ for all } \gamma \in \mathbb{R}^c, \quad \gamma^\top \mathbb{L} \text{Exp} \gamma = 0 \text{ iff } B^\top \gamma = 0. \quad (37)$$

The entropy S expressed as a function of x and the total energy E satisfy by Gibbs' fundamental thermodynamic relation

$$\frac{\partial S}{\partial x}(x, E) = -\frac{\mu}{T}, \quad \frac{\partial S}{\partial E}(x, E) = \frac{1}{T}. \quad (38)$$

This implies that for an isolated chemical reaction network (no external heat or matter flow; hence, constant energy E),

$$\frac{d}{dt}S = \frac{1}{T}\mu^\top Z\mathbb{L} \text{Exp}\left(\frac{Z^\top\mu}{RT}\right) =: \sigma \geq 0, \quad (39)$$

with equality if and only if $B^\top Z^\top\mu = N^\top\mu = 0$ (that is, if and only if the *affinities* $N^\top\mu$ of the reactions are all zero). Hence, the equilibria of the system correspond to states of minimal (that is, zero) entropy production σ , in accordance with the theory of irreversible thermodynamics [7]. By using $-S$ as a Lyapunov function, it follows, under the standard

assumption that trajectories will not converge to the boundary of the positive orthant \mathbb{R}_+^m , that any initial vector, of concentrations in the positive orthant will converge to one of these equilibria [27], [29], [30]. Note [28] that this constitutes an example of nonlinear *consensus* dynamics: If the graph of complexes is connected, then convergence takes place in a state where the elements of the vector of *complex affinities* $\delta = Z^\top\mu$ are equal.

Thermodynamic Forces and Flows and Factorization of the Dissipation Inequality

In irreversible thermodynamics, it is normally postulated [7], [31] that the irreversible entropy production can be represented as

$$\sigma = \sum_{k=1}^s F_k J_k \geq 0, \quad (40)$$

where F_k are the *thermodynamic forces* and J_k are the *thermodynamic flows* (or fluxes) in such a way that

$$\sigma = 0 \Leftrightarrow F_k = 0, \quad k = 1, \dots, s. \quad (41)$$

The examples illustrate this postulate. In the heat-exchanger example, the thermodynamic force is $F = (1/T_c) - (1/T_h)$, while the thermodynamic flow is $q = \lambda(T_h - T_c)$. Note that $\sigma = 0$ if and only if $F = 0$, that is, $T_h = T_c$. In the piston example, the thermodynamic force is $F = (P_{\text{gas}} - P_{\text{piston}}) \cdot (1/T)$, and the flow is $u v = \mu F$ for some $\mu > 0$. In the case of chemical reaction networks, the vector of thermodynamic forces F is given as $F = (1/T)N^\top\mu$ (the vector of chemical affinities is divided by temperature T). Moreover, the vector of thermodynamic flows J is given as

$$J = KB^\top \text{Exp}\frac{Z^\top\mu}{RT}, \quad (42)$$

implying that $F^\top J = \sigma$, with σ given by (39). J is also equal to the vector of the *rates of extent* of each reaction. It follows from (37) that $\sigma = 0$ if and only if $F = 0$.

From a systems and control perspective, the factorization (40) of $\sigma = (d/dt)S - (q/T)$ is closely related to the factorization of the differential dissipation inequality (S12) in (cyclo-)dissipativity theory [6], [21], [32]. For example, in the case of linear systems with quadratic supply rates, the storage function is also quadratic, and the differential dissipation inequality amounts to a linear matrix inequality [which can be factorized as in (40)]. Similarly, in *linear* irreversible thermodynamics [7], it is assumed that the vector F of thermodynamic forces and the vector J of thermodynamic flows are linearly related as

$$J = OF, \quad O = O^\top. \quad (43)$$

This relation, and especially the symmetry of the matrix O , is the celebrated *Onsager reciprocal relation* [7]. They lead to the symmetric factorization $\sigma = F^\top J = F^\top OF$.

Note that in the piston example, the thermodynamic flow J is expressed as $J = \mu F$ and is (trivially) satisfying the Onsager relation. However, the heat exchanger is *not* of this form. In fact, the thermodynamic flow $q = \lambda(T_h - T_c)$ cannot be expressed as a function of the thermodynamic force $F = (1/T_c) - (1/T_h)$ (although $q = 0$ if and only if $F = 0$). Similarly, chemical reaction networks are *not* of this form. The relationship between F and J , in this case, is *not* linear, and in most cases, J [as in (42)] cannot be expressed as a function of F . Conversely, it is shown in “Cyclo-Passive Systems as Irreversible Thermodynamic Systems” how a general cyclo-passive control system (thus satisfying a dissipation inequality), can be *embedded* in an irreversible thermodynamic formulation. This is done by introducing an extra state variable (representing entropy) and adding an internal energy, depending on this entropy.

GIBBS AND THE THERMODYNAMIC PHASE SPACE

This section marks the transition to the *geometrization* of classical thermodynamics. Gibbs’ fundamental thermodynamic relation (between the extensive and intensive variables) defines the constitutive relations (state properties) of thermodynamic systems. This naturally leads to a contact-geometric formulation (initiated by Gibbs and first explicitly stated by Hermann [33]) and entails a paradigm shift toward nonminimal systems modeling by the introduction of the thermodynamic phase space.

Gibbs’ Fundamental Thermodynamic Relation and Thermodynamic Potentials

Consider a simple thermodynamic system with variables V, P, T . The *equation of state* is an equation $f(V, P, T) = 0$ for some scalar function f . Any (V, P, T) satisfying $f(V, P, T) = 0$ is called a *state* of the thermodynamic system (see also the

Cyclo-Passive Systems as Irreversible Thermodynamic Systems

Consider a standard input-state-output system

$$\begin{aligned} \dot{x} &= f(x) + g(x)u, \quad u \in \mathbb{R}^m, \\ y &= h(x), \quad y \in \mathbb{R}^m, \end{aligned} \quad (S13)$$

where x is in some n -dimensional state-space manifold \mathcal{X} , which is assumed to be *cyclo-passive* (see “Cyclo-Dissipativity Theory”). This means that there exists a state function H , such that $(d/dt)H \leq y^\top u$, that is,

$$\frac{\partial H}{\partial x^\top}(x)f(x) =: -\rho(x) \leq 0, \quad \frac{\partial H}{\partial x^\top}(x)g(x) = h^\top(x). \quad (S14)$$

All such systems can be formulated as irreversible thermodynamic systems by defining an *extra state variable* S (interpreted as the *entropy* of the system), together with an “internal energy” $U(S)$ with $U'(S) > 0$. Namely, consider the *total energy* $E(x, S) := H(x) + U(S)$ and extend the system (S13) to

$$\begin{aligned} \dot{x} &= f(x) + g(x)u \\ \dot{S} &= \frac{\rho(x)}{U'(S)} \\ y &= h(x). \end{aligned} \quad (S15)$$

This extended system satisfies

$$\frac{d}{dt}E = \frac{d}{dt}H + \frac{d}{dt}U = -\rho(x) + y^\top u + U'(S)\frac{\rho(x)}{U'(S)} = y^\top u, \quad (S16)$$

and thus it is cyclo-lossless (satisfying the first law). Furthermore,

$$\frac{d}{dt}S = \frac{\rho(x)}{U'(S)} =: \sigma \geq 0, \quad (S17)$$

corresponding to the second law. The choice of the internal energy function $U(S)$ is rather arbitrary, with $T = U'(S) > 0$ defining “*temperature*.” One possible choice is $U(S) = T_0 S$,

corresponding to an infinite heat reservoir at constant temperature $T_0 > 0$. Note that from a thermodynamic perspective, the extended system (S15) has the structural property that the dynamics of x is independent of S . This is a common feature of port-based systems modeling [14], [15] as well as of port-Hamiltonian systems [16]–[19]. In fact, the factorization (40) of the dissipation inequality becomes most clear if the cyclo-passive system (S13) can be cast into port-Hamiltonian form,

$$\begin{aligned} \dot{x} &= \mathcal{J}(x)\frac{\partial H}{\partial x}(x) - g_R(x)R\left(g_R^\top(x)\frac{\partial H}{\partial x}(x)\right) + g(x)u \\ y &= g^\top(x)\frac{\partial H}{\partial x}(x), \end{aligned} \quad (S18)$$

for some mapping R satisfying $z^\top R(z) \geq 0$ for all vectors $z = g_R^\top(x)\frac{\partial H}{\partial x}(x)$, a skew-symmetric matrix $\mathcal{J}(x)$, and matrices $g(x), g_R(x)$. The term $-g_R(x)R\left(g_R^\top(x)\frac{\partial H}{\partial x}(x)\right)$ models *energy dissipation* (without taking into account the heat produced). Note that any port-Hamiltonian system (S18) is cyclo-passive with storage function H as the requirement $z^\top R(z) \geq 0$ implies $(d/dt)H \leq y^\top u$. Considering, as before, an additional entropy variable S and internal energy $U(S)$, the irreversible entropy production σ takes the form

$$\sigma = \frac{\partial H}{\partial x^\top}(x)g_R(x)R\left(g_R^\top(x)\frac{\partial H}{\partial x}(x)\right) \cdot \frac{1}{U'(S)} \geq 0, \quad (S19)$$

which is already in factorized form $F^\top J$ with

$$F = g_R^\top(x)\frac{\partial H}{\partial x}(x) \cdot \frac{1}{U'(S)}, \quad J = R\left(g_R^\top(x)\frac{\partial H}{\partial x}(x)\right). \quad (S20)$$

If R is a symmetric linear mapping, then the Onsager reciprocal relation (43) in the “Thermodynamic Forces and Flows, and Factorization of the Dissipation Inequality” section are satisfied.

“Basic Terminology” section). Throughout, assume that the set of states of the thermodynamic system is a 2D *submanifold* M of \mathbb{R}^3 . The first and second laws provide defined functions $E: M \rightarrow \mathbb{R}$ (*energy*) and $S: M \rightarrow \mathbb{R}$ (*entropy*). Here, E is unique up to a constant, while S is unique up to a constant under the additional assumption (compare Proposition 17 in “Cyclo-Dissipativity Theory”) that, given some ground state, there exists for any state a cyclic path through this state and the ground state satisfying [compare (23)]

$$\oint \frac{q(t)}{T(t)} dt = 0. \quad (44)$$

This will be a standing assumption throughout. Hence we may equally well represent the set of states $M \subset \mathbb{R}^3$ by the 2D submanifold $L \subset \mathbb{R}^5$, given as

$$\begin{aligned} L := \{ & (E, S, V, T, P) \mid f(V, P, T) = 0, \\ & E = E(V, P, T), S = E(V, P, T) \}. \end{aligned} \quad (45)$$

Note that, with some abuse of notation, the extra *variables* E, S are introduced, denoted by the same letters that are used for the *functions* defined previously. The ambient space \mathbb{R}^5 consisting of all the variables E, S, V, T, P is called the *thermodynamic phase space*. Furthermore (under reasonable assumptions), L can be parameterized by the extensive variables S and V , that is,

$$\begin{aligned} L := \{ & (E, S, V, T, P) \in \mathbb{R}^5 \mid E = E(S, V), T = T(S, V), \\ & P = P(S, V) \} \end{aligned} \quad (46)$$

for some functions $E(S, V)$, $T(S, V)$, $P(S, V)$. Thus, the extensive variable E and the two intensive variables T and P are expressed as functions of the remaining extensive variables S, V , which serve as coordinates for L . By the first law, $(d/dt)E = -P(d/dt)V + q$. Furthermore, by (44), there exists for any state a path through this state and the ground state such that

$$\frac{d}{dt}E = -P \frac{d}{dt}V + T \frac{d}{dt}S. \quad (47)$$

This implies that the *Gibbs’ one-form* on \mathbb{R}^5 defined as

$$dE - TdS + PdV \quad (48)$$

is *zero* restricted to L . This is called *Gibbs’ fundamental thermodynamic relation*. It implies that the submanifold L is actually given as

$$\begin{aligned} L := \{ & (E, S, V, T, P) \mid E = E(S, V), \\ & T = \frac{\partial E}{\partial S}(S, V), -P = \frac{\partial E}{\partial V}(S, V) \}. \end{aligned} \quad (49)$$

Thus, L is completely described by the energy function $E(S, V)$, hence the name *energy representation*. On the other hand, the submanifold L may be equally well parameterizable by the variables T, V , instead of by S, V . Define the *partial Legendre transform* of $E(S, V)$ with respect to S as

$$A(T, V) := E(V, S) - TS, \quad T = \frac{\partial E}{\partial S}(S, V), \quad (50)$$

where S is solved from $T = (\partial E/\partial S)(S, V)$ as a function of (T, V) . It can be verified that L parameterized by T, V is given as

$$\begin{aligned} L := \{ & (E, S, V, T, P) \mid E = A(T, V) - T \frac{\partial A}{\partial T}(T, V), \\ & S = -\frac{\partial A}{\partial T}(T, V), -P = \frac{\partial A}{\partial V}(T, V) \}. \end{aligned} \quad (51)$$

The function $A(V, T)$ is called the *Helmholtz free energy* and is one of the thermodynamic potentials [derived from $E(S, V)$] that also describe the submanifold L . For example, in the case of an ideal gas [7], [20],

$$E(S, V) = \frac{C_V e^{\frac{S}{C_V}}}{V e^{C_V}}, \quad (52)$$

where $C_V = (\partial E/\partial S)/(\partial^2 E/\partial S^2)$ denotes the heat capacity (at constant volume), and R is the universal gas constant, a partial Legendre transform $E(S, V)$ with respect to S yields the Helmholtz free energy $A(T, V)$, given as [20]

$$A(T, V) = C_V T + W - T(C_V \ln T + R \ln V + a), \quad (53)$$

for constants a (the entropy constant of the gas) and W (an integration constant). Apart from the Helmholtz free energy $A(T, V)$, there are two more thermodynamic potentials that can be obtained from $E(S, V)$ by a partial Legendre transform:

$$\begin{aligned} H(S, P) &= E(S, V) + PV, & \text{enthalpy,} & & \text{coordinates } S, P \text{ for } L \\ G(T, P) &= H(S, P) - TS, & \text{Gibbs' free energy,} & & \text{coordinates } T, P \text{ for } L \end{aligned} \quad (54)$$

Despite these different ways to parameterize L by two coordinates (corresponding to the various thermodynamic potentials as described previously), the situation is *very simple* from a *geometric* perspective. There is just *one* 2D submanifold L describing the set of states of the thermodynamic system, which is such that the Gibbs form $dE - TdS + PdV$ is zero restricted to it. The appropriate geometric (coordinate-free) formulation of this is *contact geometry* (as previously alluded to in the aforementioned Arnold quote). The Gibbs one-form defines a *contact form*, and the thermodynamic phase space \mathbb{R}^5 equipped with this contact form is called a *contact manifold*. The basic notions of contact geometry are discussed in “Contact Geometry.” The explicit use of contact geometry for the geometrization of thermodynamics was advocated in [33]–[37] (see [38] for a survey on recent developments). The use of contact geometry for thermodynamic systems from a control perspective was initiated in [39] and further explored in [40]–[42].

Aside from the aforementioned options used to parameterize the submanifold L with different sets of coordinates [corresponding to the various thermodynamic

Any dynamics of a thermodynamic system should respect the geometric structure of the thermodynamic phase space and its homogeneous symplectic extension.

potentials derivable from the energy $E(S, V)$], there is still an *alternative* way of describing the set L of thermodynamic states. This alternative starts, not with $E(S, V)$, but with the expression of the *entropy* as a function $S(E, V)$. This alternative option is also motivated from a modeling perspective [41]. In many situations (especially in chemical engineering), thermodynamic systems are formulated by first listing the *balance laws* for the extensive variable V and the mole numbers N_k of the chemical species as well as the energy E . Subsequently, the entropy is expressed as a function of these extensive variables. For a simple thermodynamic system, this leads to the *entropy representation* of the submanifold $L \subset \mathbb{R}^5$,

$$L := \{(E, S, V, T, P) \mid S = S(E, V), \frac{1}{T} = \frac{\partial S}{\partial E}(E, V), \frac{P}{T} = \frac{\partial S}{\partial V}(E, V)\}. \quad (55)$$

Starting from this entropy representation, one may then define (as in the energy representation) other thermodynamic potentials obtained by partial Legendre transforms of $S(E, V)$, corresponding to different parameterizations of L . Geometrically, the entropy representation corresponds to the one-form

$$dS - \frac{1}{T}dE - \frac{P}{T}dV \quad (56)$$

being zero on L . This one-form is obtained from the Gibbs one-form $dE - TdS + PdV$ by dividing by $-T$, and it leads to a similar (although *different*) contact-geometric description. Gibbs' fundamental thermodynamical relation (as well as the formulation of various thermodynamic potentials) is immediately extended to more general situations. For instance, in the case of multiple chemical species with mole numbers N_1, \dots, N_m and chemical potentials μ_1, \dots, μ_m , it amounts to the *extended Gibbs one-form*

$$dE - TdS + PdV - \sum_{k=1}^m \mu_k dN_k \quad (57)$$

being zero on a submanifold L of the form (in energy representation)

$$L := \{(E, S, V, N_1, \dots, N_k, T, P, \mu_1, \dots, \mu_k) \mid E = E(S, V, N_1, \dots, N_k), T = T(S, V, N_1, \dots, N_k), -P = P(S, V, N_1, \dots, N_k), \mu_i = \mu_i(S, V, N_1, \dots, N_k)\}. \quad (58)$$

See [12] for a careful derivation. This implies that

$$L := \{(E, S, V, N_1, \dots, N_k, T, P, \mu_1, \dots, \mu_k) \mid E = E(S, V, N_1, \dots, N_k), T = \frac{\partial E}{\partial S}(S, V, N_1, \dots, N_k), -P = \frac{\partial E}{\partial V}(S, V, N_1, \dots, N_k), \mu_i = \frac{\partial E}{\partial N_i}(S, V, N_1, \dots, N_k), i = 1, \dots, k\}, \quad (59)$$

with $E(S, V, N_1, \dots, N_k)$ being the energy function. By the partial Legendre transforms of $E(S, V, N_1, \dots, N_k)$, the thermodynamic potentials corresponding to other parameterizations of L are obtained. Similarly, by expressing the entropy as $S = S(E, V, N_1, \dots, N_k)$, the entropy representation of L is obtained.

A Paradigm Shift in Systems Modeling

The state space of a simple thermodynamic system is described by a 2D submanifold of the 3D space of macroscopic quantities V, P, T : one extensive and two intensive. Then (based on the first and second laws of thermodynamics), two extra extensive variables, E, S , are introduced, and the state space is equivalently described as a 2D submanifold L of \mathbb{R}^5 ; the thermodynamic phase space of the three extensive variables, E, S, V , and the two intensive variables T, P . The submanifold L defines the *constitutive relations* of the thermodynamic system (that is, the *state properties* of the system). The characterizing property of L is that it is a maximal submanifold on which the Gibbs' one-form is zero. Such manifolds are called *Legendre submanifolds*; see "Contact Geometry." In principle, any Legendre submanifold L defines possible constitutive relations. For example, the Legendre submanifold L corresponding to an *ideal gas* is different from the Legendre submanifold L corresponding to a *van der Waals gas* [20].

In general, the thermodynamic phase space is the total space of all the involved variables (extensive and intensive; one more extensive variable than intensive), and care should be taken to regard this as the state space. Instead, the *minimal* state space of the thermodynamic system is the Legendre submanifold L of the thermodynamic phase space, defining the constitutive relations of the system at hand. An (admittedly incomplete) analogy outside of the thermodynamic realm is the following. Consider a capacitor with charge Q and voltage V across it. The constitutive relations of the capacitor are specified by an energy function $E(Q)$, which defines the 1D submanifold

$$\tilde{N} = \{(Q, V) \mid V = \frac{dE}{dQ}(Q)\} \subset \mathbb{R}^2. \quad (60)$$

Q is an extensive variable and V an intensive variable. By introducing the energy E as an *extra* extensive variable, this leads to the equivalent description of the capacitor by the 1D submanifold

$$N = \left\{ (E, Q, V) \mid E = E(Q), V = \frac{dE}{dQ}(Q) \right\} \subset \mathbb{R}^3, \quad (61)$$

in the *extended* space of two extensive variables E, Q , and a single intensive variable V . The submanifold N defines a maximal submanifold of \mathbb{R}^3 restricted to which the one-form $dE - VdQ$ is zero (that is, a Legendre submanifold), analogously to the Legendre submanifold L of a simple thermodynamic system. Thus, for a capacitor, the “thermodynamic phase space” is $\{(E, Q, V) \in \mathbb{R}^3\}$, while the constitutive

Contact Geometry

As discussed in the “Gibbs and the Thermodynamic Phase Space” section, the state properties of a simple thermodynamic system with extensive variables E, S, V and intensive variables T, P are described by a 2D submanifold $L \subset \mathbb{R}^5$, which is such that the Gibbs form

$$dE - TdS + PdV \quad (S21)$$

is zero restricted to L (that is, at any point of L , the Gibbs form annihilates every tangent vector to L at this point). This is an example of *contact geometry*. In general [44], [45], a *contact manifold* M is an odd-dimensional manifold endowed with a *contact form* θ . Without going into detail, a one-form θ on a $(2n+1)$ -dimensional manifold M is a contact form if and only around any point in M one can find coordinates $\{z_0, z_1, \dots, z_n, \gamma_1, \dots, \gamma_n\}$ for M , such that

$$\theta = dz_0 - \sum_{k=1}^n \gamma_k dz_k. \quad (S22)$$

Thus the Gibbs one-form $dE - TdS + PdV$ is a contact form on the contact manifold $M = \mathbb{R}^5$.

Remark 22

In the actual definition [44] of a contact manifold, the contact form θ needs only be defined *locally*. What counts is the *contact distribution*, the $2n$ -dimensional subspace of the tangent space at any point of M defined by the kernel of the contact form θ at this point.

A *Legendre submanifold* of the contact manifold (M, θ) is a submanifold of maximal dimension restricted to which the contact form θ is zero. The dimension of any Legendre submanifold of a $(2n+1)$ -dimensional contact manifold is equal to n . In particular, the state-space manifold of a simple thermodynamic system is a 2D Legendre submanifold of $(\mathbb{R}^5, dE - TdS + PdV)$. Any Legendre submanifold can be locally represented by a *generating function* (and usually in many ways).

Proposition 23

Consider a contact manifold (M, θ) , with θ locally given by (S22). Then there exists a partitioning $\{1, \dots, n\} = I \cup J$, with

$I \cap J = \emptyset$, and locally, a generating function $F(z_i, \gamma_j)$, with z_i denoting the coordinates z_i with $i \in I$, and γ_j denoting the coordinates γ_j with $j \in J$, such that L is given as

$$L = \left\{ (z_0, z_1, \dots, z_n, \gamma_1, \dots, \gamma_n) \mid \begin{aligned} z_0 &= F - \gamma_j \frac{\partial F}{\partial \gamma_j}, z_j = -\frac{\partial F}{\partial \gamma_j}, \gamma_i = \frac{\partial F}{\partial z_i} \end{aligned} \right\}. \quad (S23)$$

Conversely, any submanifold as in (S23) is a Legendre submanifold. Furthermore, the different generating functions can be obtained from each other by a *partial Legendre transform*.

In the context of thermodynamics, the different possible choices of $F(z_i, \gamma_j)$ correspond exactly to the thermodynamic potentials, as discussed in the “Gibbs and the Thermodynamic Phase Space” section. For example, in the energy representation of a simple thermodynamic system, the generating function is the energy $E(S, V)$ (with J void) while $F(T, V)$ is the Helmholtz free energy. This can be immediately extended to the one-form

$$dE - TdS + PdV - \sum_{k=1}^m \mu_k dN_k, \quad (S24)$$

where N_k is the mole number of the k th chemical species and μ_k its chemical potential, as well as to more general one-forms corresponding to other physical cases [7].

Finally, a vector field X on a contact manifold (M, θ) is called a *contact vector field* if (with \mathbb{L}_X denoting the *Lie derivative* with respect to the vector field X)

$$\mathbb{L}_X \theta = \rho \theta \quad (S25)$$

for some scalar function ρ on M . Note that this means that X leaves the *contact distribution* invariant. The function $-\theta(X)$ is called the *contact Hamiltonian* of the contact vector field. Conversely, to any function on M , there exists a corresponding contact vector field. The expression of a contact vector field in local coordinates is somewhat complicated [38], [39]. Instead, this article focuses on the easier, homogeneous Hamiltonian vector fields on the symplectic extension of the contact manifold, which *project* to contact vector fields (see “Homogeneous Symplectic Geometry”).

relations are defined by N or, equivalently, by the energy function $E(Q)$.

FROM THERMODYNAMIC PHASE SPACE TO HAMILTONIAN DYNAMICS

Thermodynamics, as discussed so far, is basically *thermostatistics*. The first and second laws do not *define* dynamics but instead impose *constraints* on any possible dynamics. Furthermore, they lead to the definition of the extensive variables energy and entropy. The combination of the first and second laws implies Gibbs' fundamental thermodynamic relation, which characterizes all the Legendre submanifolds L defining possible constitutive relations. This implies that any dynamics should be such that the constitutive relation of

the system are respected (that is, any dynamics defined on the thermodynamic phase space should leave the Legendre submanifold L , characterizing the constitutive properties of the system, *invariant*). This can be formulated within contact geometry by a *contact vector field* with a contact Hamiltonian that is zero on L (see "Contact Geometry"). However, the next section uses one more abstraction step, which will simultaneously *resolve* some problems in the contact-geometric formulation of thermodynamic systems as well as *simplify* the representations and computations. This step will also be crucial for the definition of thermodynamic interaction ports in the "Port-Thermodynamic Systems" section. This abstraction step moves from *contact geometry* to *homogeneous symplectic geometry*.

Homogeneous Symplectic Geometry

Here we discuss how *contact geometry* (as briefly described in "Contact Geometry") can be formulated as *homogeneous symplectic geometry* by adding one dimension. This correspondence is known in differential geometry [44], [45]. Its relevance for the geometric description of thermodynamics was first advocated in [46] (primarily for uniting the energy and entropy representation) and followed up on in [47]. Start with the collection of all the *extensive variables* (that is E, S) and all of the remaining extensive variables (such as $V, N_1, \dots, N_m, \dots$). The vector of all the extensive variables will be denoted by $z = (z_0, z_1, \dots, z_n) \in \mathcal{Z}$, with \mathcal{Z} being the manifold of the extensive variables. Next consider the cotangent bundle without its zero section, denoted as $\mathcal{T}^*\mathcal{Z}$. Given the coordinates z for \mathcal{Z} , there are natural coordinates for the cotangent space denoted by $p = (p_0, p_1, \dots, p_n)$, leading to natural coordinates $(z, p) = (z_0, \dots, z_n, p_0, \dots, p_n)$ for $\mathcal{T}^*\mathcal{Z}$. In the case of thermodynamics,

$$z = (E, S, V, N_1, \dots, N_m, \dots), \quad p = (p_E, p_S, p_V, p_{N_1}, \dots, p_{N_m}, \dots). \quad (\text{S26})$$

$\mathcal{T}^*\mathcal{Z}$ is endowed with a natural one-form α (called the *Liouville form*), in the aforementioned coordinates (z, p) given as

$$\alpha = p_0 dz_0 + p_1 dz_1 + \dots + p_n dz_n. \quad (\text{S27})$$

For each $z \in \mathcal{Z}$ and each cotangent space $T_z^*\mathcal{Z}$, consider the *projective space* $\mathbb{P}(T_z^*\mathcal{Z})$, given as the set of rays in $T_z^*\mathcal{Z}$ (that is, all the nonzero multiples of a nonzero cotangent vector). The projective space $\mathbb{P}(T_z^*\mathcal{Z})$ has dimension n , and there is a canonical projection $\pi_z: T_z^*\mathcal{Z} \rightarrow \mathbb{P}(T_z^*\mathcal{Z})$, where $T_z^*\mathcal{Z}$ denotes the cotangent space *without* the zero vector. The fiber bundle of the projective spaces $\mathbb{P}(T_z^*\mathcal{Z}), z \in \mathcal{Z}$, over the base manifold \mathcal{Z} will be denoted by $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$, and it defines a *contact manifold* of dimension $2n + 1$ (one less than the dimension of $\mathcal{T}^*\mathcal{Z}$); compare [44] and [47]. Informally, whenever $p_0 \neq 0$, divide the Liouville form α in (S27) by $-p_0$ to obtain the contact form

$$\theta = dz_0 - \gamma_1 dz_1 - \dots - \gamma_n dz_n, \quad \gamma_i := \frac{p_i}{-p_0}. \quad (\text{S28})$$

Furthermore, if p_0 is zero, then divide by another $-p_i \neq 0$ (just as in the transition from energy to entropy representation). The contact manifold $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$ defines the *canonical thermodynamic phase space*. Because each cotangent space (minus the zero vector) $T_z^*\mathcal{Z}$ projects under π_z to the projective space $\mathbb{P}(T_z^*\mathcal{Z})$, this defines a total projection $\pi: \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{P}(\mathcal{T}^*\mathcal{Z})$. All of the relevant objects on the contact manifold $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$ (such as functions, Legendre submanifolds, and contact vector fields) can be shown [47] to correspond to objects on $\mathcal{T}^*\mathcal{Z}$ with an additional property of *homogeneity* in the cotangent variables p in such a way that they project under π to an object on the contact manifold $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$. Start with the homogeneity of *functions*, characterized by Euler's theorem.

Definition 24

Let $r \in \mathbb{Z}$. A function $K: \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ is called *homogeneous of degree r* (in p) if

$$K(z, \lambda p) = \lambda^r K(z, p), \quad \text{for all } \lambda \neq 0. \quad (\text{S29})$$

Theorem 25 (Euler's Homogeneous Function Theorem)

A differentiable function $K: \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ is homogeneous of degree r (in p) if and only if

$$\sum_{i=0}^n p_i \frac{\partial K}{\partial p_i}(z, p) = rK(z, p), \quad \text{for all } (z, p) \in \mathcal{T}^*\mathcal{Z}. \quad (\text{S30})$$

Furthermore, if K is homogeneous of degree r , then its derivatives $(\partial K / \partial p_i)(z, p), i = 0, 1, \dots, n$, are homogeneous of degree $r - 1$.

Obviously, a function $K: \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ that is homogeneous of degree zero in p projects to a function on the thermodynamic phase space $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$. Next consider *homogeneous Lagrangian submanifolds*. Recall that a Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$ is a maximal submanifold of $\mathcal{T}^*\mathcal{Z}$, such that $d\alpha|_{\mathcal{L}} = 0$. A Lagrangian submanifold is called *homogeneous* if, whenever $(z, p) \in \mathcal{L}$, then also $(z, \lambda p) \in \mathcal{L}$ for any $0 \neq \lambda \in \mathbb{R}$.

From Contact to Homogeneous Symplectic Geometry

Despite being directly motivated by Gibbs' fundamental thermodynamic relation, the contact-geometric view on thermodynamics has the following three shortcomings:

- 1) Switching from the energy representation $E = E(S, V)$ to the entropy representation $S = S(E, V)$ corresponds to dividing the Gibbs form $dE - TdS + PdV$ by $-T$, leading to the *new* contact form $dS - (1/T)dE - (P/T)dV$, with *new* intensive variables $(1/T), (P/T)$. Obviously, L is a Legendre submanifold for this new contact form as well. However, it leads to a *different* contact-geometric description.

Proposition 26

A submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$ is a homogeneous Lagrangian submanifold if and only if $\alpha|_{\mathcal{L}} = 0$ and it is maximal with respect to this property. For any homogeneous Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$, there exists a Legendre submanifold $L \subset \mathbb{P}(\mathcal{T}^*\mathcal{Z})$ such that $\mathcal{L} = \pi^{-1}(L)$. Conversely, for any Legendre submanifold $L \subset \mathbb{P}(\mathcal{T}^*\mathcal{Z})$, $\mathcal{L} = \pi^{-1}(L) \subset \mathcal{T}^*\mathcal{Z}$ is a homogeneous Lagrangian submanifold.

Thus, Legendre submanifolds L of the contact manifold $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$ (the canonical thermodynamic phase space) correspond to homogeneous Lagrangian submanifolds \mathcal{L} of $\mathcal{T}^*\mathcal{Z}$. Furthermore, let $F(z_i, \gamma_j)$, with $\{1, \dots, n\} = I \cup J, I \cap J = \emptyset$ being a generating function for the Legendre submanifold $L \subset \mathbb{P}(\mathcal{T}^*\mathcal{Z})$ (compare "Contact Geometry"). Then, a generating function for the corresponding homogeneous Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$ [such that $\mathcal{L} = \pi^{-1}(L)$], is given by

$$G(z_i, p_0, p_j) = -p_0 F\left(z_i, \frac{p_j}{-p_0}\right), \quad (\text{S31})$$

in the sense that

$$\mathcal{L} = \left\{ (z, p) \mid q_0 = -\frac{\partial G}{\partial p_0}, q_j = -\frac{\partial G}{\partial p_j}, p_i = \frac{\partial G}{\partial q_i} \right\}. \quad (\text{S32})$$

For *dynamics*, recall that for any function $K : \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$, the *Hamiltonian vector field* X_K on $\mathcal{T}^*\mathcal{Z}$ is defined by the standard Hamiltonian equations

$$\dot{z}_i = \frac{\partial K}{\partial p_i}(z, p), \quad \dot{p}_i = -\frac{\partial K}{\partial z_i}(z, p), \quad i = 0, 1, \dots, n. \quad (\text{S33})$$

Now impose on the Hamiltonians $K : \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ the condition that they are homogeneous of degree one in p , that is, $K(q, \lambda p) = \lambda K(q, p)$ for all $\lambda \neq 0$.

Proposition 27

If $K : \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ is homogeneous of degree one in p , then its Hamiltonian vector field X_K is such that (\mathbb{L}_X denotes the Lie derivative with respect to the vector field X)

- 2) The contact-geometric approach does not make a clear distinction between extensive and intensive variables: Given a contact form θ , there are many Darboux coordinates [as in (S22) in "Contact Geometry"].
- 3) Computations in contact geometry tend to be involved, especially when *dynamics* is concerned.

The way to solve these problems is to *extend* contact manifolds by one extra dimension to *symplectic* manifolds (cotangent bundles) with an added *homogeneity* structure. For a simple thermodynamic system with extensive variables E, S, V and intensive variables $T, -P$, this amounts to replacing the intensive variables $T, -P$ in the energy representation with their *homogeneous coordinates* p_E, p_S, p_V with $p_E \neq 0$, that is,

$$\mathbb{L}_{X_K} \alpha = 0. \quad (\text{S34})$$

Conversely, if $\mathbb{L}_X \alpha = 0$, then $X = X_K$, where the function $K := \alpha(X)$ is homogeneous of degree one in p .

Hamiltonians $K : \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ that are homogeneous of degree one in p and their corresponding Hamiltonian vector fields X_K will be called *homogeneous*. Any homogeneous Hamiltonian vector field projects to a *contact vector field* $X_{\hat{K}}$ with contact Hamiltonian \hat{K} on the thermodynamic phase space $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$. Conversely, any contact vector field on $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$ is the projection of a homogeneous Hamiltonian vector field on $\mathcal{T}^*\mathcal{Z}$ [47]. As the state properties of the thermodynamic system are specified by a Legendre submanifold $L \subset \mathbb{P}(\mathcal{T}^*\mathcal{Z})$ (Gibbs' fundamental relation) or its corresponding homogeneous Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$, any dynamics of a thermodynamic system should leave \mathcal{L} invariant. This is elegantly characterized as follows.

Proposition 28

A homogeneous Hamiltonian vector field X_K leaves a homogeneous Lagrangian submanifold \mathcal{L} invariant if and only if K is zero on \mathcal{L} .

Remark 29

A similar statement holds for the corresponding Legendre submanifold L : The contact vector field leaves L invariant if and only if its contact Hamiltonian is zero on L .

Finally, [47] notes that the Poisson bracket of two homogeneous Hamiltonian functions is homogeneous, and that the Lie bracket of two homogeneous Hamiltonian vector fields on $\mathcal{T}^*\mathcal{Z}$ is homogeneous. This allows for establishing a Lie-algebraic theory for verifying the *controllability* and *observability* of port-thermodynamic systems [47], [S8].

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$$T = \frac{p_s}{-p_E}, \quad -P = \frac{p_V}{-p_E}, \quad (62)$$

as well as to expressing the intensive variables $(1/T), (P/T)$ in the entropy representation as

$$\frac{1}{T} = \frac{p_E}{-p_s}, \quad \frac{P}{T} = \frac{p_V}{-p_s}. \quad (63)$$

In this way, the *two* Gibbs one-forms $(dE'TdS + PdV)$ and $dS - (1/T)dE - (P/T)dV$ are replaced by a *single* symmetric expression (namely, the *Liouville one-form*),

$$p_E dE + p_s dS + p_V dV. \quad (64)$$

The Liouville one-form is the canonical one-form on the cotangent bundle $T^*\mathbb{R}^3$, with \mathbb{R}^3 being the space of extensive variables E, S, V , with cotangent space coordinates p_E, p_s, p_V . By the definition of homogeneous coordinates, the vector (p_E, p_s, p_V) is different from the 0-vector, implying that the space $\{(E, S, V, p_E, p_s, p_V)\}$ is the cotangent bundle $T^*\mathbb{R}^3$ minus its zero section. Furthermore, replacing the intensive variables with their homogeneous coordinates, the 2D Legendre submanifold L is replaced with the 3D submanifold $\mathcal{L} \subset T^*\mathbb{R}^3$,

$$\mathcal{L} = \left\{ (E, S, V, p_E, p_s, p_V) \mid \left(E, S, V, \frac{p_s}{-p_E}, \frac{p_V}{-p_E} \right) \in L \right\}. \quad (65)$$

Note that \mathcal{L} is a *Lagrangian* submanifold, which is, moreover, *homogeneous* in the sense that whenever $(E, S, V, p_E, p_s, p_V) \in \mathcal{L}$, then $(E, S, V, \lambda p_E, \lambda p_s, \lambda p_V) \in \mathcal{L}$ for any nonzero $\lambda \in \mathbb{R}$. Such homogeneous Lagrangian submanifolds are fully characterized as maximal manifolds restricted to which the Liouville one-form $p_E dE + p_s dS + p_V dV$ is zero (see “Homogeneous Symplectic Geometry”). In this way, the first two disadvantages of the contact geometry formulation (the difference between energy and entropy representation, and the lack of a clear distinction between extensive and intensive variables) are resolved. As explained in “Homogeneous Symplectic Geometry,” this “symplectization” of contact manifolds (by adding one extra dimension to the space of intensive variables) has clear computational advantages as well. All of the computations become standard operations in Hamiltonian dynamics. In the words of Arnold [43]: One is advised to calculate symplectically (but to think, rather, in terms of contact geometry). The symplectization of contact manifolds is known in differential geometry [44], [45]. Within a thermodynamics context, its use was first advocated in [46] and followed up on in [47].

Homogeneous Hamiltonian Dynamics

Consider a simple thermodynamic system with extensive variables $(E, S, V) \in \mathbb{R}^3$. Also consider the cotangent bundle $T^*\mathbb{R}^3$ minus its zero section, with coordinates E, S, V, p_E, p_s, p_V . For any function $K: T^*\mathbb{R}^3 \rightarrow \mathbb{R}$, the standard Hamiltonian differential equations are

$$\begin{aligned} \dot{E} &= \frac{\partial K}{\partial p_E}(E, S, V, p_E, p_s, p_V) \\ \dot{S} &= \frac{\partial K}{\partial p_s}(E, S, V, p_E, p_s, p_V) \\ \dot{V} &= \frac{\partial K}{\partial p_V}(E, S, V, p_E, p_s, p_V) \\ \dot{p}_E &= -\frac{\partial K}{\partial E}(E, S, V, p_E, p_s, p_V) \\ \dot{p}_s &= -\frac{\partial K}{\partial S}(E, S, V, p_E, p_s, p_V) \\ \dot{p}_V &= -\frac{\partial K}{\partial V}(E, S, V, p_E, p_s, p_V). \end{aligned} \quad (66)$$

Impose the condition that K is homogeneous of degree one in p , that is,

$$K(E, S, V, \lambda p_E, \lambda p_s, \lambda p_V) = \lambda K(E, S, V, p_E, p_s, p_V), \text{ for all } \lambda \neq 0. \quad (67)$$

For such K , the Hamiltonian differential equations (66) project to a *contact vector field* on the contact manifold with coordinates (in the energy representation) $E, S, V, T, -P$. Conversely, any contact vector field is the projection of a Hamiltonian dynamics with homogeneous Hamiltonian K . The same holds for the entropy representation $E, S, V, (1/T), (P/T)$. The generalities concerning this are discussed in “Homogeneous Symplectic Geometry.” The Hamiltonian differential equations for homogeneous K respect the structure of $T^*\mathbb{R}^3$ (as captured by its Liouville form). Furthermore, they leave invariant the homogeneous Lagrangian submanifold \mathcal{L} (specifying the state properties of the thermodynamic system) if and only if K is zero on \mathcal{L} . It follows that any Hamiltonian dynamics generated by a function K that is 1) homogeneous of degree one in p and 2) zero on \mathcal{L} , is a *feasible dynamics* for the thermodynamic system. This will be the starting point for the definition of *port-thermodynamic systems* in the next section.

Interestingly, although the Hamiltonians in the formulation of mechanical systems represent *total energy*, the Hamiltonians K in this section are *dimensionless* (in the sense of dimensional analysis). Together with the earlier observation that the dynamics of a thermodynamic system are captured by the dynamics *restricted* to the invariant homogeneous Lagrangian submanifold, this emphasizes that the Hamiltonian dynamics (66) has a rather different interpretation than in the standard Hamiltonian formulation of mechanical (or other physical) systems. Another context where the same phenomena occur is *optimal control*; see “Digression on Optimal Control and Homogeneous Symplectic Geometry.”

PORT-THERMODYNAMIC SYSTEMS

As argued in the previous section (see [47] for additional information), any dynamics of a thermodynamic system should respect the geometric structure of the thermodynamic phase space and its homogeneous symplectic extension. Furthermore, it should leave invariant the Legendre

Digression on Optimal Control and Homogeneous Symplectic Geometry

It was recently shown in [S9] and [S10] how Pontryagin's Maximum principle naturally leads to *contact geometry*. This stems from the fact that the vector of costate variables in the Mayer formulation of an optimal control problem is a *separating vector*, which can be arbitrarily scaled. The purpose of this digression is to highlight the initial homogeneous symplectic formulation, already implicitly present in [S9] and [S10]. This sheds additional light on the *abnormal case* in optimal control. Consider the optimal control problem of minimizing for fixed final-time τ the cost criterion

$$\int_0^\tau L(x(t), u(t)) dt, \quad x \in \mathbb{R}^n \quad (\text{S35})$$

over all input functions $u : [0, \tau] \rightarrow \mathbb{R}^m$ for the dynamics $\dot{x} = f(x, u)$ with given initial condition $x(0)$. The first step is to define an additional state variable x_0 , such that $\dot{x}_0 = L(x, u)$, $x_0(0) = 0$. This converts the optimal control problem into the "Mayer problem" of minimizing $x_0(\tau)$ over the augmented dynamics

$$\begin{aligned} \dot{x}_0 &= L(x, u), & x_0(0) &= 0 \\ \dot{x} &= f(x, u), & x(0) &\text{ given.} \end{aligned} \quad (\text{S36})$$

Next define the pseudo-Hamiltonian $H : \mathcal{T}^*\mathbb{R}^{n+1} \times \mathbb{R}^m \rightarrow \mathbb{R}$ as

$$H(x_0, x, \lambda_0, \lambda, u) = \lambda^\top f(x, u) + \lambda_0 L(x, u). \quad (\text{S37})$$

By construction, H is homogeneous of degree one in $(\lambda_0, \lambda) \in \mathbb{R}^{n+1}$. The corresponding homogeneous Hamiltonian vector field X_H (parameterized by u) is

$$\begin{aligned} \dot{x}_0 &= L(x, u) \\ \dot{x} &= f(x, u) \\ \dot{\lambda}_0 &= 0 \\ \dot{\lambda}^\top &= -\lambda^\top \frac{\partial f(x, u)}{\partial x} - \lambda_0 \frac{\partial L(x, u)}{\partial x}. \end{aligned} \quad (\text{S38})$$

In the first two lines of (S38), the original augmented dynamics (S36) is recovered. As H does not depend on x_0 , it follows that λ_0 is *constant* (with $\lambda_0 = 0$ corresponding to the so-called *abnormal case*). Here, $(\lambda_0, \lambda) \in \mathbb{R}^{n+1}$ should be understood as a vector of *homogeneous coordinates* for the cotangent spaces to the state-space manifold with coordinates (x_0, x) . Hence, for $\lambda_0 \neq 0$, the standard costate variables are defined as

$$\gamma := \frac{\lambda}{-\lambda_0}, \quad (\text{S39})$$

resulting in the differential equations of Pontryagin's Maximum principle

$$\begin{aligned} \dot{x}_0 &= L(x, u) \\ \dot{x} &= f(x, u) \\ \dot{\gamma}^\top &= -\gamma^\top \frac{\partial f}{\partial x}(x, u) + \frac{\partial L}{\partial x^\top}(x, u) \end{aligned} \quad (\text{S40})$$

(where the equation for \dot{x}_0 could be omitted as well). As noted in [S9] and [S10], the dynamics (S40) are a *contact vector field* (parameterized by u) on the odd-dimensional contact manifold with coordinates x_0, x, γ and the contact form $dx_0 - \sum_{i=1}^n \gamma_i dx_i$.

Alternatively (from a homogeneous symplectic perspective,) (S40) is the *projection* of the homogeneous Hamiltonian vector field (S38). Thus, the differential equations of Pontryagin's Maximum principle can be understood as arising from the choice of the "intensive" variables $\gamma = (\lambda/\lambda_0)$ in case the constant λ_0 is different from zero (the "normal" case). In the *abnormal case* where $\lambda_0 = 0$, the differential equations of the Maximum principle are most easily given in the form

$$\begin{aligned} \dot{x}_0 &= L(x, u) \\ \dot{x} &= f(x, u) \\ \dot{\lambda}^\top &= -\lambda^\top \frac{\partial f}{\partial x}(x, u). \end{aligned} \quad (\text{S41})$$

On the other hand, note that this does *not* correspond to a choice of "intensive variables," such as $\tilde{\gamma} = (\lambda_0, \lambda_2, \dots, \lambda_n)^\top \cdot (1/\lambda_1)$. This explains the peculiar form of the differential equations of the Maximum principle in the abnormal case.

Furthermore, note that for the *infinite-horizon* ($\tau \rightarrow \infty$) optimal control problem, the stationary Hamilton–Jacobi–Bellman equation corresponds to a homogeneous Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathbb{R}^{n+1}$ with generating function $-\lambda_0 V(x)$, where V is Bellman's *value function*, that is,

$$\mathcal{L} = \left\{ (x_0, x, \lambda_0, \lambda) \mid x_0 = V(x), \lambda = -\lambda_0 \frac{\partial V}{\partial x}(x) \right\}. \quad (\text{S42})$$

The minimum of H on \mathcal{L} with respect to u is zero:

$$\min_u H\left(V(x), x, \lambda_0, -\lambda_0 \frac{\partial V}{\partial x}(x), u\right) = 0, \quad (\text{S43})$$

thus implying that \mathcal{L} is invariant. See also [S11] for an interesting connection between the contact-geometric formulation of the Maximum principle in optimal control and the maximum entropy maximum principle of Callen [S2].

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submanifold of the thermodynamic phase space (or equivalently, the corresponding Lagrangian submanifold of the homogeneous symplectic extension). This section adopts the same generality and notation as in “Contact Geometry” and “Homogeneous Symplectic Geometry,” where the space of all the extensive variables is denoted by \mathcal{Z} , the symplectic extension by $\mathcal{T}^*\mathcal{Z}$ with coordinates (z, p) , and the thermodynamic phase space by $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$. For instance, in a simple thermodynamic system, \mathcal{Z} is \mathbb{R}^3 with coordinates E, S, V , $\mathcal{T}^*\mathcal{Z}$ has coordinates E, S, V, p_E, p_S, p_V , while the coordinates for $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$ are $E, S, V, T, -P$ (energy representation) or $E, S, V, (1/T), (P/T)$ (entropy representation). Because of its simplicity (and because it allows for defining, in a natural way, *ports*), this section emphasizes the description of the symplectic extension $\mathcal{T}^*\mathcal{Z}$. See [47] for details on the resulting projection to the thermodynamic phase space $\mathbb{P}(\mathcal{T}^*\mathcal{Z})$.

Consider a thermodynamic system with constitutive relations (state properties) specified by a homogeneous Lagrangian submanifold $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$. Respecting the geometric structure of the symplectic extension $\mathcal{T}^*\mathcal{Z}$ means that the dynamics is a Hamiltonian vector field X_K on $\mathcal{T}^*\mathcal{Z}$, with K homogeneous of degree one in the p variables. According to “Homogeneous Symplectic Geometry,” any such vector field leaves the Liouville form on $\mathcal{T}^*\mathcal{Z}$ invariant. Furthermore, X_K leaves the homogeneous Lagrangian submanifold \mathcal{L} invariant if and only if K restricted to \mathcal{L} is zero. Finally, K is split into two parts, that is,

$$K^a + K^c u, \quad u \in \mathbb{R}^m. \quad (68)$$

$K^a: \mathcal{T}^*\mathcal{Z} \rightarrow \mathbb{R}$ is the homogeneous Hamiltonian corresponding to the autonomous dynamics due to internal equilibrium conditions. Furthermore, $K^c = (K_1^c, \dots, K_m^c)$ is a row vector of homogeneous Hamiltonians (called *control* or *interaction* Hamiltonians) corresponding to the dynamics arising from interactions with the surroundings of the system. This second part of the dynamics is affinely parameterized by a vector u of *control* or *input* variables [see, however, Example 12 (Mass-Spring-Damper System) for a nonaffine dependency on u]. As K is homogeneous of degree one in p and zero on \mathcal{L} for all $u \in \mathbb{R}^m$, this simply means that all the $(m+1)$ functions K^a, K_1^c, \dots, K_m^c are homogeneous of degree one in p and zero on \mathcal{L} . Invoking Theorem 25 (Euler’s Homogeneous Function Theorem) in “Homogeneous Symplectic Geometry” implies that

$$\begin{aligned} K^a &= p_0 \frac{\partial K^a}{\partial p_0} + p_1 \frac{\partial K^a}{\partial p_1} + \dots + p_n \frac{\partial K^a}{\partial p_n} \\ K^c &= p_0 \frac{\partial K^c}{\partial p_0} + p_1 \frac{\partial K^c}{\partial p_1} + \dots + p_n \frac{\partial K^c}{\partial p_n}, \end{aligned} \quad (69)$$

where the partial derivatives $\partial K^a/\partial p_i$ as well as $\partial K_j^c/\partial p_i$, $j = 1, \dots, m$, for $i = 0, 1, \dots, n$ are all homogeneous of degree zero in the p variables. (Note that this does *not* necessarily mean these functions are independent of p ; although, of course, this is an important special case.)

There are two more constraints on K^a , as imposed by the first and second laws. As the energy and entropy variables E, S are among the extensive variables z_0, z_1, \dots, z_n , take $E = z_0, S = z_1$. With this convention, the internal dynamics X_{K^a} have $\dot{E} = \partial K^a/\partial p_0$. Hence, by the first law, the energy of the system should be conserved if there is no interaction with the surroundings (that is, $u = 0$), implying that necessarily $(\partial K^a/\partial p_0)|_{\mathcal{L}} = 0$. Similarly, $\partial K^a/\partial p_1$ is equal to \dot{S} in the internal dynamics X_{K^a} . Hence by the second law of thermodynamics, $(\partial K^a/\partial p_1)|_{\mathcal{L}} \geq 0$. See [37] for a related (although different) perspective within a contact geometry setting. These additional constraints do not hold for the control (interaction) Hamiltonians K_j^c , $j = 1, \dots, m$. The control Hamiltonians may be utilized to define natural *output* variables conjugated to the inputs u . The first option is to define the m -dimensional row vector

$$y_p = \frac{\partial K^c}{\partial p_0} \quad (70)$$

with the subscript p in y_p representing *power*. It follows that along the dynamics X_K on \mathcal{L} with $K = K^a + K^c u$,

$$\frac{d}{dt} E = y_p u, \quad (71)$$

and thus, y_p is the vector of *power-conjugate* (passive) outputs corresponding to the input vector u . The pair (u, y_p) is called the *power port* of the system. Similarly, by defining the m -dimensional row vector (*ef* for “entropy flow”)

$$y_{ef} = \frac{\partial K^c}{\partial p_1}, \quad (72)$$

it follows that along the dynamics X_K on \mathcal{L} ,

$$\frac{d}{dt} S \geq y_{ef} u. \quad (73)$$

Hence, y_{ef} is the output vector that is conjugate to u in terms of *entropy flow*. The pair (u, y_{ef}) is called the *entropy flow port* of the system. Note that one could also define the outputs that are conjugated to u for other extensive variables. This will lead to other types of ports [compare the Example 10 (Chemical Reaction Networks) on chemical reaction networks at the end of this section]. This is summarized in the following definition of a *port-thermodynamic system* [47].

Definition 6

Consider the space of extensive variables \mathcal{Z} . A port-thermodynamic system is a pair (\mathcal{L}, K) , where $\mathcal{L} \subset \mathcal{T}^*\mathcal{Z}$ is a homogeneous Lagrangian submanifold describing the state properties, and $K = K^a + K^c u$, $u \in \mathbb{R}^m$ is a Hamiltonian on $\mathcal{T}^*\mathcal{Z}$ that is homogeneous of degree one in p and zero on \mathcal{L} . Let $z = (z_0, z_1, \dots, z_n)$, with $z_0 = E$ (energy), and $z_1 = S$ (entropy). Then K additionally satisfies $(\partial K^a/\partial p_0)|_{\mathcal{L}} = 0$ and $(\partial K^a/\partial p_1)|_{\mathcal{L}} \geq 0$. Furthermore, the power-conjugate output is defined as $y_p = \partial K^c/\partial p_0$, and the entropy flow-conjugate output is defined as $y_{ef} = \partial K^c/\partial p_1$.

Note that by the correspondence between contact geometry and homogeneous symplectic geometry, any port-thermodynamic system on $\mathcal{T}^*\mathcal{Z}$ corresponds to a system on the thermodynamic phase space $\mathbb{P}(T^*\mathcal{Z})$ (which can be represented either in energy or entropy representation). The following examples, partly taken from [47], illustrate the definition of a port-thermodynamic system. As mentioned previously, the Hamiltonian K is *dimensionless*. On the other hand, the *contact Hamiltonian* \hat{K} of its projected dynamics has the dimension of *power* in the case of the energy representation and the dimension of *entropy flow* in the case of the entropy representation.

Example 7 (Heat Compartment)

Consider a heat compartment that exchanges heat with its surroundings. Its thermodynamic properties are described by the extensive variables S (entropy) and E (internal energy), with E expressed as a function $E = E(S)$ of S , and $E'(S) \geq 0$. Its state properties are given by the homogeneous Lagrangian submanifold

$$\mathcal{L} = \{(E, S, p_E, p_S) \mid E = E(S), p_S = -p_E E'(S)\}, \quad (74)$$

corresponding to the generating function $-p_E E(S)$. As there are no internal dynamics, K^a is absent. Hence, taking u as the *entropy flow* corresponds to considering the homogeneous Hamiltonian

$$K^c(E, S, p_E, p_S) = p_S + p_E E'(S), \quad (75)$$

which is zero on \mathcal{L} . This yields the dynamics on \mathcal{L} , entailing energy and entropy balance,

$$\begin{aligned} \dot{E} &= E'(S)u & \dot{p}_E &= 0 \\ \dot{S} &= u & \dot{p}_S &= -p_E E''(S)u, \end{aligned} \quad (76)$$

with power-conjugate output y_p equal to $E'(S)$. Note that $\gamma = p_S / -p_E$ is the temperature T , and the projected dynamics on the thermodynamic phase space $\mathbb{P}(T^*\mathbb{R}^2)$ is

$$\begin{aligned} \dot{E} &= E'(S)u \\ \dot{S} &= u \\ \dot{T} &= -\frac{\dot{p}_S}{p_E} = E''(S)u. \end{aligned} \quad (77)$$

This is a contact vector field (see ‘‘Contact Geometry’’) with contact Hamiltonian $\hat{K}^c(E, S, T) = T - E'(S)$, which leaves the Legendre submanifold

$$L = \{(E, S, T) \in \mathbb{P}(T^*\mathbb{R}^2) \mid E = E(S), T = E'(S)\} \quad (78)$$

invariant. Alternatively, if we take instead the incoming *heat flow* as input v , then the Hamiltonian is given by

$$K(E, S, p_E, p_S) = \left(p_S \frac{1}{E'(S)} + p_E \right) v, \quad (79)$$

leading to the entropy flow-conjugate output y_{ef} , given by the reciprocal temperature $y_{ef} = 1/E'(S)$.

Example 8 (Mass-Spring-Damper System)

This is an example that normally would not be considered a thermodynamic system. Nevertheless, in view of the dissipation of energy due to the damper, there is a thermodynamic component (namely, the heat irreversibly produced by the damper). Consider a mass-spring-damper system in 1D motion composed of a mass m with momentum π , linear spring with stiffness k and extension w , and linear damper with damping coefficient d . To take into account the thermal energy and the entropy production arising from the heat produced by the damper, the variables of the mechanical system are augmented with an entropy variable S and internal energy $U(S)$, with $U'(S) > 0$. For instance, if the system is isothermal (that is, in thermodynamic equilibrium with a thermostat at temperature T_0), the internal energy is $U(S) = T_0 S$. This leads to the total set of extensive variables w, π, S, E , with $E = (1/2)kw^2 + (\pi^2/2m) + U(S)$ (total energy). The state properties of the system are described by the homogeneous Lagrangian submanifold \mathcal{L} with the generating function (in energy representation)

$$-p_E \left(\frac{1}{2}kw^2 + \frac{\pi^2}{2m} + U(S) \right) \quad (80)$$

defining the state properties

$$\mathcal{L} = \left\{ (E, S, w, \pi, p_E, p_S, p_w, p_\pi) \mid E = \frac{1}{2}kw^2 + \frac{\pi^2}{2m} + U(S), \right. \\ \left. p_w = -p_E kw, p_\pi = -p_E \frac{\pi}{m}, p_S = -p_E U'(S) \right\}. \quad (81)$$

The dynamics are given by the following homogeneous Hamiltonian (zero on \mathcal{L}),

$$K = p_w \frac{\pi}{m} + p_\pi \left(-kw - d \frac{\pi}{m} \right) + p_S \frac{d \left(\frac{\pi}{m} \right)^2}{U'(S)} + \left(p_\pi + p_E \frac{\pi}{m} \right) u, \quad (82)$$

where u is an external force. The power-conjugate output $y_p = \pi/m$ is the velocity of the mass.

Example 9 (Gas-Piston-Damper System)

Consider a gas in a thermally isolated cylinder closed by a piston. Assuming the thermodynamic properties of the system are covered by the properties of the gas, the system is completely analogous to the previous example, replacing w with volume V and the partial energy $(1/2)kw^2 + U(S)$ with the internal energy $U(S, V)$ of the gas. The dynamics of the gas-piston-damper system (with the piston actuated by a force u) is given by the Hamiltonian

$$K = p_V \frac{\pi}{m} + p_\pi \left(-\frac{\partial U}{\partial V} - d \frac{\pi}{m} \right) + p_S \frac{d \left(\frac{\pi}{m} \right)^2}{\partial S} + \left(p_\pi + p_E \frac{\pi}{m} \right) u, \quad (83)$$

where the power-conjugate output $y_p = \pi/m$ is the velocity of the piston.

Example 10 (Chemical Reaction Networks)

Consider a chemical reaction network in entropy representation, as in the “Chemical Reaction Networks” section. Thus, the entropy S is represented as a function $S = S(E, x)$ of the energy E and the vector of chemical concentrations x . The homogeneous Lagrangian submanifold describing the state properties of the reaction network is

$$\mathcal{L} = \left\{ (E, S, x, p_E, p_S, p_x) \mid S = S(E, x), p_E = -p_S \frac{\partial S}{\partial E}(E, x), \right. \\ \left. p_x = -p_S \frac{\partial S}{\partial x}(E, x) \right\}, \quad (84)$$

with $(\partial S / \partial x)(E, x) = -(\mu / T)$, $(\partial S / \partial E)(E, x) = 1/T$. The internal dynamics of the chemical reaction network are generated by the following Hamiltonian (homogeneous of degree one in (p_E, p_S, p_x) , and zero on \mathcal{L}),

$$K^a = -\left(p_x + p_S \frac{\partial S}{\partial x}(E, x) \right)^T Z \mathbb{L} \text{Exp} \frac{-Z^T}{R} \frac{\partial S}{\partial x}(E, x). \quad (85)$$

The control Hamiltonian

$$K^c = p_S \frac{\partial S}{\partial E}(E, x) + p_E, \quad (86)$$

corresponds to a *heat flow* input, and an entropy flow-conjugate output $y_{ef} = (\partial S / \partial E)(x, E)$ equal to the *reciprocal temperature*. Another possible choice is

$$K^c = p_S \frac{\partial S}{\partial x_i}(E, x) + p_{x_i}. \quad (87)$$

This corresponds to material in/outflow of the i th chemical species, and an entropy flow-conjugate output $y_{ef} = (\partial S / \partial x_i)(E, x)$ which is given by the chemical potential μ_i of the i th chemical species divided by $-T$.

In this last example, the internal dynamics is a first-order dynamics that converges irreversibly to a state where the elements of the vector of complex affinities $Z^T(\partial S / \partial x)$ are equal (and thus, in the kernel of \mathbb{L} , compare [27] and [28]). In the prior two examples (mass-spring-damper system and gas-piston-damper system), this is different. Although there is an irreversible increase of entropy due to the damper action, there is also an

internal dynamics corresponding to the oscillatory transformation of kinetic energy into potential energy and, conversely, that leads to second-order dynamics. Thus, the internal dynamics of thermodynamic systems do *not* necessarily correspond to irreversible dynamics.

In *composite*, nonhomogeneous, thermodynamic systems (compare the “Basic Terminology” section), there is typically no *single* energy or entropy. The constraints on the internal dynamics are different: The *sum* of the energies must be conserved. Likewise, the *sum* of the entropies must be increasing. A simple example is the following (see [47] for further information).

Example 11 (Heat Exchanger)

Consider a heat exchanger (as depicted in Figure 6) composed of two heat compartments, as in Example 7 (Heat Compartment). There is heat flow from the hot to the cold compartment through a conducting wall, according to Fourier’s law. The three extensive variables are S_1, S_2 (entropies of the two compartments), and E (total internal energy). The state properties are described by the homogeneous Lagrangian submanifold

$$\mathcal{L} = \left\{ (S_1, S_2, E, p_{S_1}, p_{S_2}, p_E) \mid E = E_1(S_1) + E_2(S_2), \right. \\ \left. p_{S_1} = -p_E E'_1(S_1), p_{S_2} = -p_E E'_2(S_2) \right\}, \quad (88)$$

corresponding to the generating function $-p_E(E_1(S_1) + E_2(S_2))$, with E_1, E_2 being the internal energies of the two compartments. The internal dynamics of the heat exchanger are given by the homogeneous Hamiltonian

$$K^a = \lambda \left(\frac{1}{E'_1(S_1)} - \frac{1}{E'_2(S_2)} \right) (p_{S_1} E'_2(S_2) - p_{S_2} E'_1(S_1)), \quad (89)$$

with λ Fourier’s conduction coefficient. The total entropy on \mathcal{L} satisfies

$$\frac{d}{dt}(S_1 + S_2) = \lambda \left(\frac{1}{E'_1(S_1)} - \frac{1}{E'_2(S_2)} \right) (E'_2(S_2) - E'_1(S_1)) \geq 0. \quad (90)$$

Note that this can be generalized to heat conduction in solids [48].

Comparison With Port-Hamiltonian Formulation

The definition of a port-thermodynamic system (Definition 6) is distinctly different from the standard definition of a *port-Hamiltonian system* [17]–[19]. Although they both involve Hamiltonian dynamics, the interpretation of the Hamiltonian dynamics and the Hamiltonian function in both formulations is different. In port-Hamiltonian systems, the Hamiltonian is given by the total stored energy (as in classical Hamiltonian mechanics), while the Hamiltonian K in the homogeneous Hamiltonian dynamics (66) is a dimensionless quantity. Furthermore, port-thermodynamic systems inherently constitute a nonminimal state-space

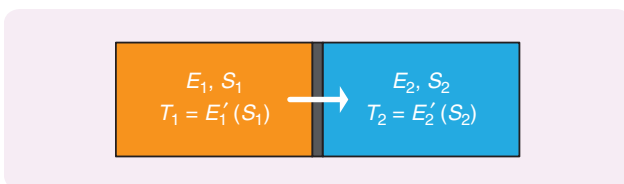


FIGURE 6 A heat exchanger.

representation in which a homogeneous Lagrangian (or Legendre) submanifold is left invariant by the dynamics. This Lagrangian submanifold specifies the constitutive relations including the energy expression of the thermodynamic system.

In a comparison of the two definitions, the Hamiltonian function in a port-Hamiltonian system corresponds to the homogeneous Lagrangian submanifold in a port-thermodynamic system. On the other hand, the Hamiltonian of a port-thermodynamic system covers the interconnection structure of the system (which in the port-Hamiltonian formulation is expressed by a Poisson or Dirac structure). As shown in “Cyclo-Passive Systems as Irreversible Thermodynamic Systems,” any port-Hamiltonian system can be embedded in an irreversible thermodynamic system by including entropy as an extra extensive variable. By lifting the dynamics of the extensive variables (the state variables of the port-Hamiltonian system plus the entropy and energy) to the cotangent bundle, this leads to a port-thermodynamic system. Finally, note that the definition of port-thermodynamic systems not only allows for power ports (as is the case for port-Hamiltonian systems) but also for *entropy flow* ports.

It is emphasized that the port-Hamiltonian formalism is not broad enough to cover general thermodynamic systems [49]. This was one of the motivations for the definition of port-thermodynamic systems in [47]. The insufficiency of the standard port-Hamiltonian framework for thermodynamic systems modeling has already been suggested by the irreversible thermodynamic formulation of port-Hamiltonian systems (compare “Cyclo-Passive Systems as Irreversible Thermodynamic Systems”), where the dynamics of the state variable x is independent of the entropy. More directly, it is illustrated by the example of the heat exchanger whose formulation as a port-thermodynamic system was given previously in Example 11 (Heat Exchanger). The heat exchanger can also be represented as

$$\begin{bmatrix} \dot{S}_1 \\ \dot{S}_2 \end{bmatrix} = \begin{bmatrix} -\lambda \frac{E_1'(S_1) - E_2'(S_2)}{E_1'(S_1)} \\ \lambda \frac{E_1'(S_1) - E_2'(S_2)}{E_2'(S_2)} \end{bmatrix} = \begin{bmatrix} 0 & \lambda \left(\frac{1}{E_1'(S_1)} - \frac{1}{E_2'(S_2)} \right) \\ -\lambda \left(\frac{1}{E_1'(S_1)} - \frac{1}{E_2'(S_2)} \right) & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial E}{\partial S_1} \\ \frac{\partial E}{\partial S_2} \end{bmatrix}, \quad (91)$$

where $E(S_1, S_2) := E_1(S_1) + E_2(S_2)$ is the total energy. This is a *quasi*-port-Hamiltonian formulation: Although the 2×2 matrix in (91) is skew symmetric (and thus, the conservation of energy E is guaranteed), it does *not* define a proper Poisson structure on the state space \mathbb{R}^2 with coordinates S_1, S_2 . The reason is that this matrix does not directly depend on the state variables S_1, S_2 , but instead *through* the temperatures $E_1'(S_1), E_2'(S_2)$. Alternatively, the dynamics in (91) are *nonlinear* in $E_1'(S_1) = \partial E / \partial S_1$,

$E_2'(S_2) = \partial E / \partial S_2$ (as opposed to the standard definition of a Hamiltonian vector field). Note that this nonlinear dependence is key to the crucial property $(d/dt)(S_1 + S_2) \geq 0$ (increase of total entropy). This observation has given rise to the alternative notion of *irreversible port-Hamiltonian systems* [49].

Equivalent Parameterizations of the Dynamics

As discussed in the “A Paradigm Shift in Systems Modeling” section, Gibbs’ fundamental thermodynamic relation leads to the consideration of *nonminimal* state-space representations, namely, the thermodynamic phase space consisting of all the extensive and intensive variables. The minimal state space is a Legendre submanifold L specifying the state properties of the thermodynamic system. In the same way, the definition of a port-thermodynamic system entails dynamics on the *whole* thermodynamic phase space (or equivalently, its symplectic extension), leaving invariant the Legendre submanifold L (or the homogeneous Lagrangian submanifold \mathcal{L}). This means that the dynamics on L can be parameterized in different ways, either by extensive or intensive variables (or by mixtures of them). This is similar to the use of the various thermodynamical potentials used to describe L (see the “Gibbs and the Thermodynamic Phase Space” section). Conversely, these different parameterizations of the dynamics are over-arched by the dynamics on the whole thermodynamic phase space or its symplectic extension.

Specifically, consider a port-thermodynamic system with homogeneous Hamiltonian dynamics X_K on $\mathcal{T}^* \mathcal{Z}$ with natural coordinates (z, p) , where $K = K^a + K^c u$ is zero on the homogeneous Lagrangian submanifold \mathcal{L} . As before, $z_0 = E, z_1 = S$, and $p_0 = p_E, p_1 = p_S$. The simplest parameterizations of the dynamics on \mathcal{L} are obtained by considering the dynamics of the extensive variables z_1, \dots, z_n [corresponding to the energy representation $E = E(z_1, z_2, \dots, z_n)$], or the dynamics of z_0, z_2, \dots, z_n [corresponding to the entropy representation $S = S(z_0, z_2, \dots, z_n)$]. The dynamics can be parameterized equally well by considering the dynamics of the *intensive* variables $\gamma_1, \dots, \gamma_n$ obtained from the coextensive variables $p = (p_0, p_1, \dots, p_n)$. For example, in the energy representation, the intensive variables are

$$\gamma_1 = \frac{p_1}{-p_0}, \dots, \gamma_n = \frac{p_n}{-p_0}, \quad (92)$$

which when restricted to \mathcal{L} are equal to

$$\frac{\partial E}{\partial z_1}(z_1, \dots, z_n), \dots, \frac{\partial E}{\partial z_n}(z_1, \dots, z_n). \quad (93)$$

Denote $\tilde{z} := (z_1, \dots, z_n)^\top$ and $\gamma = (\gamma_1, \dots, \gamma_n)^\top$. Then, (93) defines a mapping

$$\tilde{z} \mapsto \gamma = \frac{\partial E}{\partial \tilde{z}}(\tilde{z}). \quad (94)$$

Assuming the $n \times n$ Hessian matrix $(\partial^2 E / \partial \bar{z}^2)(\bar{z})$ to be invertible, define the Legendre transform $E^*(\gamma)$ of the function $E(\bar{z})$, which satisfies

$$\gamma = \frac{\partial E}{\partial \bar{z}}(\bar{z}), \quad \bar{z} = \frac{\partial E^*}{\partial \gamma}(\gamma), \quad \frac{\partial^2 E}{\partial \bar{z}^2}(\bar{z}) = \left(\frac{\partial^2 E^*}{\partial \gamma^2}(\gamma) \right)^{-1}. \quad (95)$$

These equalities allow for rewriting the dynamics of the n extensive variables \bar{z} into dynamics of the n intensive variables γ as

$$\frac{\partial^2 E^*}{\partial \gamma^2}(\gamma) \dot{\gamma} = \dot{\bar{z}}. \quad (96)$$

A very simple example was previously provided in Example 7 (Heat Compartment) (77). The dynamics on \mathcal{L} are described by $\dot{S} = u$ or $\dot{\gamma} = E''(S)u$, where the extensive variable S (entropy) is related to the intensive variable $\gamma = T$ (temperature) by $\gamma = E'(S)$. A more involved case is in Example 9 (Gas-Piston-Damper System). For simplicity, let $d = 0$ (no damping). The dynamics on \mathcal{L} are parameterized by the extensive variables S, V, π as

$$\begin{aligned} \dot{S} &= 0 \\ \dot{V} &= \frac{\pi}{m} \\ \dot{\pi} &= -\frac{\partial U}{\partial V} + u. \end{aligned} \quad (97)$$

The dynamics expressed in the intensive variables $\gamma_1 = \partial U / \partial S$ (temperature), $\gamma_2 = \partial U / \partial V$ (minus the pressure), and $\gamma_3 = \pi / m$ (velocity) can be computed as

$$\begin{aligned} \dot{\gamma}_1 &= \gamma_3 \frac{\partial^2 U}{\partial S \partial V} \\ \dot{\gamma}_2 &= \gamma_3 \frac{\partial^2 U}{\partial V^2} \\ \dot{\gamma}_3 &= -\frac{1}{m} \gamma_2 + u. \end{aligned} \quad (98)$$

This can be written fully in terms of γ by computing the Legendre transform $U^*(\gamma_1, \gamma_2)$ of $U(S, V)$ and using the fact that the Hessian matrix of U is the inverse of the Hessian matrix of U^* , compare (95). Similar computations can be performed to obtain a parameterization of the dynamics on \mathcal{L} in terms of the intensive variables corresponding to the entropy representation. In general, the transformation of the dynamics in extensive variables into the description of the dynamics in intensive variables is similar to the transformation of port-Hamiltonian dynamics in energy variables to its description in coenergy variables [18]. This is also closely related to the (generalized) Brayton–Moser formulation of physical systems [18], [50].

PORTS AND INTERCONNECTIONS

The definition of ports enables the interconnection of thermodynamic systems so as to obtain complex systems from

simpler building blocks. Start with the case of *power-port* interconnections of port-thermodynamic systems, corresponding to energy flow exchange. This is the standard situation considered in the physical network modeling of interconnected systems, especially in port-based modeling theory and port-Hamiltonian systems [15], [18]. Take two port-thermodynamic systems, with input vectors u_1 , and u_2 , and the *power-conjugate* outputs y_{p1} , y_{p2} (as introduced in the definition of port-thermodynamic systems). Consider interconnection constraints satisfying the *power conservation* property

$$y_{p1}^\top u_1 + y_{p2}^\top u_2 = 0, \quad (99)$$

in accordance with the first law. More generally, in the case of an additional *external* power port with variables u , y_p , consider the power-conserving interconnection constraints satisfying

$$y_{p1}^\top u_1 + y_{p2}^\top u_2 + y_p^\top u = 0. \quad (100)$$

Example 12 (Mass-Spring-Damper System)

This example demonstrates that the thermodynamic formulation of the system in Example 8 (Mass-Spring-Damper System) also results from the interconnection of its three subsystems: mass, spring, and damper. The same analysis applies (*mutatis mutandis*) to the system presented in Example 9 (Gas-Piston-Damper System).

- 1) *Mass subsystem* (excluding irrelevant entropy): The state properties are given by the homogeneous Lagrangian submanifold

$$\mathcal{L}_m = \left\{ (\kappa, \pi, p_\kappa, p_\pi) \mid \kappa = \frac{\pi^2}{2m}, p_\pi = -p_\kappa \frac{\pi}{m} \right\}, \quad (101)$$

with energy κ (kinetic energy), momentum π , and dynamics generated by the Hamiltonian

$$K_m = \left(p_\kappa \frac{\pi}{m} + p_\pi \right) u_m \quad (102)$$

corresponding to $\dot{\pi} = u_m$, $y_m = \pi / m$.

- 2) *Spring subsystem* (again excluding irrelevant entropy): The state properties are given by

$$\mathcal{L}_s = \left\{ (P, w, p_P, p_w) \mid P = \frac{1}{2} k w^2, p_w = -p_P k w \right\}, \quad (103)$$

with energy P (elastic energy), spring extension w , and dynamics generated by the Hamiltonian

$$K_s = (p_P k w + p_w) u_s \quad (104)$$

corresponding to $\dot{w} = u_s$, $y_s = k w$.

- 3) *Damper subsystem*: The state properties are given by

$$\mathcal{L}_d = \{ (U, S) \mid U = U(S), p_S = -p_U U'(S) \}, \quad (105)$$

with the entropy S and an internal energy $U(S)$, while the dynamics are generated by the Hamiltonian

$$K_d = \left(p_U + p_S \frac{1}{U'(S)} \right) du_d^2, \quad (106)$$

with d the damping constant and power-conjugate output $y_d := du_d$ equal to the damping force.

Now interconnect the three subsystems via their power ports (u_m, y_m) , (u_s, y_s) , (u_d, y_d) as

$$u_m = -y_s - y_d, \quad u_s = y_m = u_d. \quad (107)$$

This results (after setting $p_\kappa = p_p = p_U$) in a port-thermodynamic system with total Hamiltonian $K_m + K_s + K_d$ equal to the Hamiltonian K^a [as obtained previously in (82)].

Interconnection via entropy flow ports is *different*, as by the second law, the total entropy flow is not necessarily zero but greater than or equal to zero. This is illustrated by the following example.

Example 13

The heat exchanger of in Example 11 (Heat Exchanger) (as depicted in Figure 6) can be modeled as the interconnection of two heat compartments [as in Example 7 (Heat Compartment)] via their entropy flow ports (v_i, y_{efi}) , where $y_{efi} = 1/E'(S_i)$, $i = 1, 2$. The interconnection (corresponding to the conducting wall) is defined as $v_1 = -v_2 = \lambda((1/y_{ef2}) - (1/y_{ef1}))$, with $\lambda > 0$ Fourier's conduction coefficient. This interconnection does not conserve entropy, but instead corresponds to its increase

$$y_{ef1}v_1 + y_{ef2}v_2 = \lambda \left(\frac{1}{y_{ef2}} - \frac{1}{y_{ef1}} \right) (y_{ef1} - y_{ef2}) \geq 0. \quad (108)$$

(The reader is referred to [47] for a more elaborate treatment.)

CONCLUSION

The emphasis of this article was on two aspects: a clear *cyclo-dissipativity* interpretation of classical macroscopic thermodynamics and a *geometric* (coordinate-free) formulation of the state properties of a thermodynamic system and its dynamics (through contact and homogeneous symplectic geometry). Both aspects are considered essential in aligning thermodynamics with modern systems and control theory as well as in the integration of thermodynamics in unified frameworks for complex systems modeling for control. This underlines the engineering motivation and background of classical thermodynamics and its relevance for advanced control engineering.

One of the benefits of the discussed geometric formulation of thermodynamic systems is the definition of interaction ports of thermodynamic systems. This allows for a compositional modeling of complex multiphysics systems, including thermal behavior. It also provides a starting point for *control by interconnection* of such systems

by interconnecting a given plant thermodynamic system with a controller thermodynamic system. Another venue for control is the "shaping by feedback" of the port-thermodynamic system into another port-thermodynamic system with desired characteristics [51]. This line of research continues and extends similar approaches in passivity-based control and port-Hamiltonian systems. Note that the transformation of a port-thermodynamic system not only entails energy shaping and power flow routing, but may also include "entropy shaping" and "routing of entropy flow."

As mentioned previously, a major research challenge lies in the connection of thermodynamics with information theory aimed at uniting control strategies based on energy shaping and power flow routing with an information processing perspective. Many other aspects of thermodynamics and their implications for systems and control were not discussed in this article. The maximum entropy principle (using the concavity of the entropy function), the stability analysis of forced equilibria of nonequilibrium thermodynamic systems by minimal irreversible entropy production [7], and mesoscopic thermodynamics [52] seem to be especially relevant for systems analysis and control.

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