

# Chapter 2

## Thermodynamics

### 2.1 Introduction

The First Law of Thermodynamics is a statement of the existence of a property called Energy which is a state function that is independent of the path and, in the context of mechanics, a conservative (potential) function such as gravity. The Second Law of Thermodynamics guarantees the existence and uniqueness of stable equilibrium states of a large class of nonlinear systems. Exergy is the availability, the maximum amount of work that can be extracted reversibly from an energy flow with respect to a dead state, as well as the unifying metric of choice to develop the equations of motion and the power flow models. Local equilibrium, a way to utilize the mathematics of equilibrium thermodynamics, is applied to nonequilibrium irreversible system models to produce nonlinear rate and power equations. The First and Second Laws of Thermodynamics are reviewed in detail and applied to these models to generate energy and entropy balance equations. In turn, these balance equations are written in rate equation form in order to produce the exergy rate equation which provides the fundamental connection to Hamiltonian mechanics and stability analysis. The development of this chapter will follow and combine the writings of Gyftopoulos [43], Prigogine [4], and Scott [44, 45].

### 2.2 First Law (Energy)

The First Law of Thermodynamics is a statement of the existence of a property called Energy [43]. Energy is a state function,  $\mathcal{E}$ , that is path independent which implies a conservative function in the context of mechanics. An example of path-independent work is adiabatic reversible work where no heat is exchanged with the environment: raising and lowering a mass in a friction-less way referred to as a weight process. In this process, no entropy is transferred or created in this reversible system; then

$$\mathcal{E}_2 - \mathcal{E}_1 = -\mathcal{W}_{12}, \quad (2.1)$$

where

$\mathcal{E}_i$  = energy at state  $i$  of the system,  
 $\mathcal{W}_{12}$  = work done by the system between states 1 and 2.

A work process transfers energy but transfers no entropy. Irreversible entropy can be produced within a system during a work process. A work-only process is an adiabatic process.

A corollary of the First Law that is often referred to as the First Law is

$$d\mathcal{E} = \delta Q - \delta W, \quad (2.2)$$

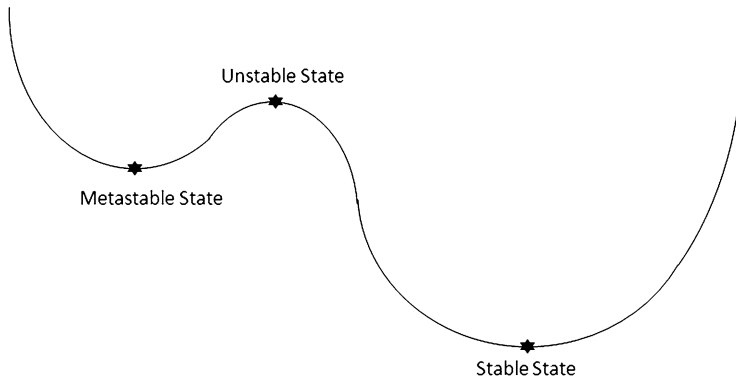
where

$d\mathcal{E}$ —change of state, path-independent,  
 $\delta Q$ —flow of heat, path-dependent,  
 $\delta W$ —work done by the system, path-dependent,

which is the energy balance equation for work and heat interactions and identified as the conservation of energy. Note that energy is conserved by the First Law, so energy is not a useful economic metric since economics is the allocation of scarce resources. Exergy will be shown to be an ideal economic metric since it is consumed and most likely scarce.

### 2.3 Second Law (Stability/Entropy/Available Work)

The Second Law of Thermodynamics is a statement of the existence and uniqueness of stable equilibrium states and that reversible processes connect these states together with any arbitrary state. A nonequilibrium state is one that changes spontaneously as a function of time, that is, a state that evolves as time goes on without any effects on or interactions with any systems in the environment [43]. An example is the time evolution of a undamped or damped system with initial conditions away from an equilibrium state. An equilibrium state is defined as a state that does not change with time while the system is isolated from all other systems in the environment: a state that does not change spontaneously [43]. Specifically, an isolated system cannot exchange energy, entropy, etc. with any other system. An unstable equilibrium state is an equilibrium state that can be caused to proceed spontaneously to a sequence of entirely different states by means of a minute and short-lived interaction that has an infinitesimal temporary effect on the state of the environment [43]. An unstable state is effectively the same as an unstable state described by Lyapunov stability and will be expanded upon when discussing static stability and dynamic stability in the following chapters. A metastable equilibrium state is an equilibrium state that can be altered without leaving net effects in the environment of the system and without changing the values of amounts of constituents and parameters to an incompatible set of values, but this can be done only by means of interactions that have a finite temporary effect on the state of the environment [43]. The metastable equilibrium state is described by Lyapunov stability as a locally asymptotically stable



**Fig. 2.1** Equilibrium states (potential energy)

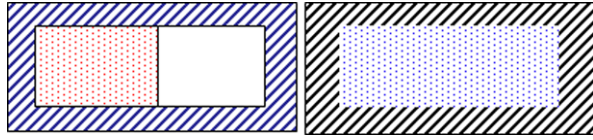
state because damping is intrinsic to the system due to entropy production. A stable equilibrium state is an equilibrium state that can be altered to a different state only by interactions that either leave net effects in the environment of the system or change the values of amounts of constituents and parameters to an incompatible set of values [43]. The stable equilibrium state is described by Lyapunov stability as a globally asymptotically stable state because damping is intrinsic which leads to the minimum energy state of the system due to entropy production. These equilibrium states are presented in Fig. 2.1. We will introduce additional definitions of equilibrium states that do not include entropy production in later chapters which are referred to as Lagrange and Lyapunov stable when defining static and dynamic stabilities.

**Second Law States** Among all the states of a system with a given value of the energy and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state; and, starting from any state of a system, it is possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process [43]. Notice that the Second Law states that a stable equilibrium state exists for each value of the energy while mechanics defines only a stable state at the minimum energy state or ground state. The stable equilibrium states of thermodynamics have three requirements:

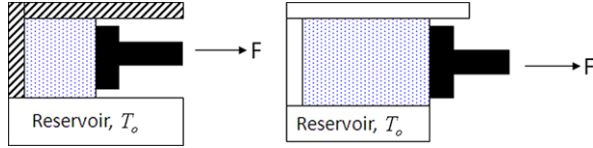
1. Each stable equilibrium state is the state of lowest energy among all the states with the same values of entropy, volume, and parameters of the system.
2. Each stable equilibrium state is the state of highest entropy among all the states with the same values of energy, volume, and parameters of the system.
3. Temperature is positive and increasing with energy which implies the energy versus entropy curve for stable equilibrium states is convex.

All three requirements imply that the state of the system is static which leads to why classical thermodynamics is referred to as Equilibrium Thermodynamics or Thermostatistics. Although the energy and entropy balance equations apply to any

**Fig. 2.2** Expansion of gas: adiabatic irreversible expansion



**Fig. 2.3** Expansion of gas: reversible expansion



states of the system, when applying Equilibrium Thermodynamics, the system is effectively moving between equilibrium states since many of the quantities such as temperature and pressure are only defined for equilibrium states.

The Second Law helps differentiate between reversible and irreversible processes and provides a limit on the maximum amount of work that can be done with an energy flow. A process is reversible if the system and its environment can be restored to their initial states, except for differences of small order of magnitude than the maximum changes that occur during the process; otherwise the process is irreversible [43]. The classic example used to discuss the differences between irreversible and reversible processes is the expansion of a gas. Figure 2.2 shows the irreversible expansion of a gas by pulling a divider from a container that is half full to create a container with the gas fully expanded into the entire container.

This is a process that is operating between two equilibrium states. The system changes due to a constraint change: pulling the divider. To return the gas to its original condition will require additional work: irreversible. Figure 2.3 shows the reversible expansion of a gas by letting the gas do work against a friction-less piston at a constant temperature. This work can be reversed to return the gas to its original state: reversible.

To mathematically quantify these examples, the available work is defined as  $\Omega$ , where

$$\Omega_2 - \Omega_1 = -(\mathcal{W}_{12})_{\text{rev}}, \quad (\mathcal{W}_{12})_{\text{rev}} \geq \mathcal{W}_{12}, \quad (2.3)$$

and the maximum available work occurs when the process is reversible. Otherwise, part of the work is lost through entropy production

$$d\mathcal{S} \equiv c_R(d\mathcal{E} - d\Omega), \quad (2.4)$$

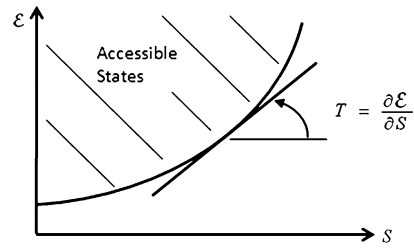
and entropy is given the symbol  $\mathcal{S}$ , while  $c_R$  is a scaling factor. An interesting case of entropy production occurs for adiabatic processes such as shown in Fig. 2.2. For a reversible adiabatic process,

$$(d\mathcal{S})_{\text{rev}} = 0. \quad (2.5)$$

For an irreversible adiabatic process,

$$(d\mathcal{S})_{\text{irrev}} \geq 0. \quad (2.6)$$

**Fig. 2.4** Energy versus entropy curve



Returning to the three requirements, a corollary to the Second Law emerges from this discussion: At a stable equilibrium state, the entropy will be at its maximum value for fixed values of energy, number of particles, and constraints [43]. Also, the energy will be at a minimum value, the temperature is positive and increasing, plus the energy versus entropy curve for stable equilibrium states is convex. This is presented in Fig. 2.4.

A reversible process can be defined as interacting systems quasi-statically passing only through stable equilibrium states. The heat flowing between these interacting systems during a reversible process is

$$\begin{aligned}
 dQ &= \delta Q_{\text{rev}} = T dS \\
 &= d\mathcal{E} + \delta W_{\text{rev}} \\
 &= d\mathcal{E} + dW \\
 &= d\mathcal{E} - d\Omega \\
 &= \frac{1}{C_R} dS,
 \end{aligned} \tag{2.7}$$

where  $T$  is temperature. The entropy production during a reversible process is

$$dS = \frac{dQ}{T}; \quad S = 0 = \oint \frac{dQ}{T}. \tag{2.8}$$

The entropy production during an irreversible process is [4]

$$dS \geq \frac{dQ}{T}, \tag{2.9}$$

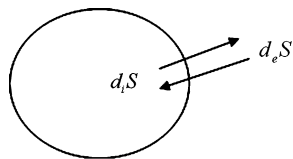
where

$$dS = d_e S + d_i S \tag{2.10}$$

with

$d_e S$ —entropy change due to exchange of energy and matter (entropy flux),  
 $d_i S$ —entropy change due to irreversible processes.

This is the entropy balance equation. The combination of the energy and entropy balance equations is the basic set of tools used to solve most problems in thermodynamics. These will be used to derive the exergy rate equation.

**Fig. 2.5** Entropy changes

The entropy fluxes and irreversible entropy production are presented in Fig. 2.5. The irreversible entropy production can be written as

$$d_i S = \sum_k \mathcal{F}_k d\mathcal{X}_k \geq 0, \quad (2.11)$$

where

$$\begin{aligned} \mathcal{F}_k &\text{---} k\text{th thermodynamics force,} \\ \mathcal{X}_k &\text{---} k\text{th thermodynamics flow,} \end{aligned}$$

which appears to be a scaled power flow or work rate (discussed in the next chapter). The scaling factor is  $1/T_0$ .

## 2.4 Equilibrium Thermodynamics (Reversible/Irreversible Processes)

Returning to reversible processes one more time, in classical thermodynamics (equilibrium thermodynamics [4]), it is assumed that every irreversible transformation that occurs in nature can also be achieved through a reversible process (guaranteed by the Second Law) where

$$S_2 = S_1 + \int_1^2 \frac{dQ}{T}, \quad (2.12)$$

and Fig. 2.6 presents a sketch of the processes of Figs. 2.2 and 2.3; note that entropy is a state function. This is the real strength of equilibrium thermodynamics. By analyzing systems in this way, one can calculate the changes in thermodynamic states via a straightforward procedure even if the processes may be quite complex such as an internal combustion engine. The amount of work that can be done by a cyclic heat engine, extracting work from a flow of heat, is limited by the Carnot efficiency of a reversible cycle (refer to [4]).

A reversible cyclic process can be analyzed with the First and Second Laws applied as

$dU = T dS - p d\bar{V}$	Energy balance equation
$dU = d\mathcal{E}$	Internal energy
$T dS = dQ$	Entropy balance equation
$p d\bar{V} = dW$	$p$ —pressure, $\bar{V}$ —volume

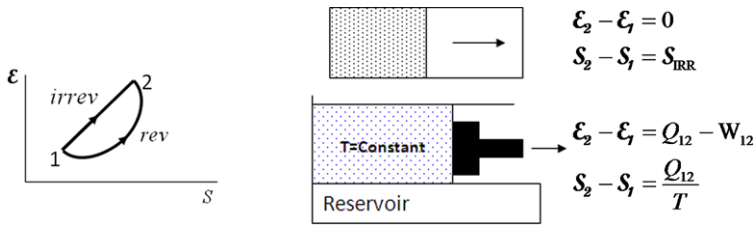


Fig. 2.6 Equilibrium thermodynamics

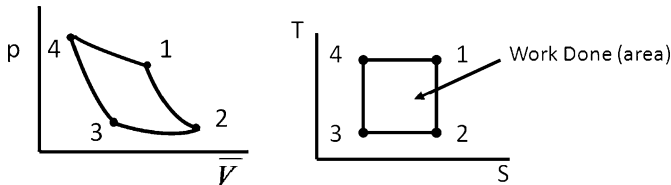


Fig. 2.7 Reversible cyclic work

Then

$$\oint dU = 0 = \oint T dS - \oint p d\bar{V}. \quad (2.13)$$

This implies that

$$\oint T dS = \oint p d\bar{V} \quad (2.14)$$

where a uniform temperature exists throughout the system during a process, and the change in energy over a cycle is zero since energy is a state function. The work done over a cycle shown in Fig. 2.7 can be calculated by the  $pV$ -work or the area in the  $TS$  plane since they balance one another. We will expand on this cyclic balance in later chapters to demonstrate the concepts of limit cycles and power flow balances that arise from nonequilibrium irreversible thermodynamic systems.

## 2.5 Local Equilibrium (Nonequilibrium Thermodynamics; Energy, Entropy, and Exergy Rate Equations)

The analysis of nonequilibrium irreversible systems is a complicated problem which requires large numbers of parameters and variables to accomplish. Quantities such as temperature and pressure are only defined in the context of equilibrium thermodynamics. The concept of “Local Equilibrium” can be used to extend the application of equilibrium thermodynamic quantities to nonequilibrium irreversible thermodynamic systems by providing well-defined quantities locally within each elemental

volume. To be more specific, temperature is not uniform but is well defined locally. In general, for nonequilibrium systems, we can define thermodynamic quantities in terms of densities where thermodynamic variables become functions of position and time. For this purpose, the time dependence which produces rate equations is retained.

The energy balance equation [45] in terms of rate of change of energy is

$$\dot{\mathcal{E}} = \sum_j \dot{Q}_j + \sum_k \dot{W}_k + \sum_l \dot{m}_l (h_l + ke_l + pe_l + \dots). \quad (2.15)$$

The term on the left represents the rate at which energy is changing within the system. The heat entering or leaving the system is given by  $\dot{Q}_j$ , and the work done by or on the system is given by  $\dot{W}_k$ . Next, material can enter or leave the system by  $\dot{m}_l$  that includes enthalpy,  $h$ , kinetic and potential energies,  $ke$ ,  $pe$ , etc. In addition, each term is “summed” over an arbitrary number of entry and exit locations  $j, k, l$ .

The entropy balance equation (2.10) in terms of rate of change of entropy is

$$\dot{S} = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_k \dot{m}_k s_k + \dot{S}_i = \dot{S}_e + \dot{S}_i, \quad \dot{S}_i = \sum_l \mathcal{F}_l \dot{\mathcal{X}}_l \geq 0 \quad (2.16)$$

where the left-hand term is the rate entropy changes within the system, and the right-hand terms represent, in order, the rate heat conducts entropy to and from the system and the rate material carries it in or out. These two terms can be combined into one term  $\dot{S}_e$ , the entropy exchanged (either positive or negative) with the environment.  $\dot{S}_i$  is the irreversible entropy production rate within the system which is the sum of all the entropy changes due to the irreversible flows  $\dot{\mathcal{X}}_l$  with respect to each corresponding thermodynamic force  $\mathcal{F}_l$  (also see (2.11)).

Next, for systems with a constant environmental temperature, a thermodynamic quantity, called the availability function which has the same form as the Helmholtz free energy function, is defined as [4]

$$\mathcal{E} = \mathcal{E} - T_0 S, \quad (2.17)$$

where  $T_0$  is the reference environmental temperature. The availability function is the system exergy, described as the maximum theoretically available energy that can do work with respect to a given state via a reversible process. Exergy is also known as negative entropy [44, 45]. By taking the time derivative of the exergy in (2.17) and substituting into the expressions for energy (2.15) and entropy rates (2.16) results in the exergy rate equation

$$\dot{\mathcal{E}} = \dot{\mathcal{E}} - T_0 \dot{S} = \sum_j \left(1 - \frac{T_0}{T_j}\right) \dot{Q}_j + \sum_k (\dot{W}_k - p_0 \dot{V}) + \sum_l \dot{m}_l \zeta_l^{\text{flow}} - T_0 \dot{S}_i \quad (2.18)$$



where  $\dot{\mathcal{E}}$  is the rate at which exergy stored within the system is changing. The terms on the right, in order, define the rate exergy is carried in/out by: (i) heat, (ii) work (less any work the system does on the environment at constant environmental pressure  $p_0$  if the system volume  $\bar{V}$  changes), and (iii) by the material (or quantity known as flow exergy). The final term,  $T_0\dot{S}_i$ , is the rate exergy is destroyed (dissipated) within the system. This is the thermodynamic equation that will be used throughout the rest of the book to support the development of necessary and sufficient conditions for stability for a class of nonlinear systems, Hamiltonian natural systems. During the development of the connections between thermodynamics and Hamiltonian mechanics section, the class of thermodynamic systems that are analyzed will be adiabatic irreversible work processes: systems that have work done on them and have internal irreversible entropy production in the form of dissipation mechanisms that transfer no heat or material.

## 2.6 Chapter Summary

This chapter reviewed the basic concepts of thermodynamics required to support the development of necessary and sufficient conditions for stability of a class of nonlinear systems, Hamiltonian natural systems and adiabatic irreversible work processes. The First Law of Thermodynamics was reviewed and related to conservative mechanical systems. The Second Law of Thermodynamics was reviewed and related to the equilibrium of nonlinear systems. Exergy was defined as the availability, the maximum amount of work that can be extracted reversibly from an energy flow, and presented as the unifying metric of choice to develop the equations of motion and the power flow models. Local equilibrium was explained as a way to utilize the mathematics of equilibrium thermodynamics in order to analyze nonequilibrium irreversible system models to produce nonlinear rate and power equations.

To be more specific, the First and Second Laws of Thermodynamics were applied to system models to generate energy and entropy balance equations. In turn, these balance equations were written in rate equation form to produce the exergy rate equation which provides the fundamental connection to Hamiltonian mechanics and stability analysis.

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Utilizing Exergy, Entropy, Static and Dynamic Stability,  
and Lyapunov Analysis

Robinett III, R.D.; Wilson, D.G.

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