

# *Appendices*

# *Appendix A*

## *Crash-Course on*

### *Equilibrium*

#### *Thermodynamics*

To provide the background for beyond-equilibrium thermodynamics, we here outline the fundamentals of equilibrium thermodynamics. Equilibrium thermodynamics must not only be obtained as a special case of any acceptable nonequilibrium generalization but, through its shining example, it also elucidates the wide scope, the emphasis on universal relationships, and the advantages of a systematic postulational approach to beyond-equilibrium thermodynamics. This appendix is based on an article<sup>1</sup> that was written with exactly the same motivation, providing the background of equilibrium thermodynamics for a special issue of the *Journal of Non-Newtonian Fluid Mechanics* on nonequilibrium thermodynamics.<sup>2</sup> The article, in turn, was based on the famous textbook on equilibrium thermodynamics by Callen.<sup>3</sup> Callen's book, finally, is based on authority. The present crash-course on thermodynamics hence

<sup>1</sup> Jongschaap & Öttinger, *J. Non-Newtonian Fluid Mech.* 96 (2001) 5.

<sup>2</sup> See issue no. 1–2 in *J. Non-Newtonian Fluid Mech.* 96 (2001).

<sup>3</sup> Callen, *Thermodynamics* (Wiley, 1985).

follows Callen's clearly structured and widely accepted postulational approach as closely as possible.

## A.1 APPROACH AND SCOPE

In this appendix, we summarize the key elements of equilibrium thermodynamics. Although this subject is covered by many textbooks and is a standard part of the education in most branches of science and engineering and despite the fact that the treatment of common applications such as the calculation of the efficiency of engines, phase behavior, chemical equilibria, and so forth are well understood and frequently used, we nevertheless undertake this effort because there still seems to be no consensus on the treatment of the fundamentals of thermodynamics. It is not only for pedagogical reasons that in the various textbooks many starting points and many routes of the further developments can be found. For example, one could take the traditional considerations of Carnot, Kelvin, and Clausius, which led to the famous formulations of the second law as a starting point, or Boltzmann's famous statistical expression of the entropy,  $S = k_B \ln \Omega$ , or the asymmetrical time evolution of irreversible processes, or the topology of the space of equilibrium states, or the information theoretical method, or the treatment based on the Clausius-Duhem inequality of rational thermodynamics.

We do not attempt to discuss any of the above-mentioned approaches here. We just present a concise and consistent outline of the fundamentals of equilibrium thermodynamics. For that purpose, we follow the well-known textbook of Callen, which is widely accepted as a brilliant source on the foundations of equilibrium thermodynamics. The present appendix is a selection of annotated quotations from this book.

We follow the treatment of Callen as closely as possible, with a special emphasis on fundamental concepts and principles. We focus on elucidating the structural elements of thermodynamics and the principles of statistical mechanics. How can we make sure that our selection of the key elements of thermodynamics and statistical mechanics indeed is in the spirit of Callen? For thermodynamics, we have Chapter 12 of his book as a valuable guide, in which the basic principles are summarized and generalized to systems including magnetic, electric, elastic, and other effects. The increasing importance that he ascribed to statistical mechanics is evident from the inclusion of six chapters on this topic in going from the first edition (1960) to the second edition (1985) of his book. For further details on specific subjects, the reader is of course referred to Callen's book or to alternative sources, such as Reichl's comprehensive textbook.<sup>4</sup>

Although we assume that most of that readers of this book are familiar with equilibrium thermodynamics to an extent that he or she would feel that a crash-course on thermodynamics is hardly necessary, we would still like to offer some basic remarks

<sup>4</sup>Reichl, *Modern Course in Statistical Physics* (University of Texas, 1980).

in the spirit of Callen's book by citing from his introduction. He describes the scope of thermodynamics as follows:

Thermodynamics (...) neither claims a unique domain of systems over which it asserts primacy, nor does it introduce a new fundamental law analogue to Newton's or Maxwell's equations. In contrast to the specialty of mechanics and electromagnetism, the hallmark of thermodynamics is generality. Generality first in the sense that thermodynamics applies to all types of systems in macroscopic aggregation, and second in the sense that thermodynamics does not predict specific numerical values for observable quantities. Instead thermodynamics sets limits (*inequalities*) on permissible physical processes, and it establishes relationships among apparently unrelated properties.

Callen characterizes thermodynamics as a universal framework for the macroscopic description of matter:

whereas thermodynamics is not based on a new and particular law of nature, it instead reflects a commonality of universal feature of *all* laws. In brief, *thermodynamics is the study of restriction on the possible properties of matter that follows from the symmetry properties of the fundamental laws of physics.*

Extrapolating Callen's point of view, beyond-equilibrium thermodynamics should be a general theory of the properties of matter, including the dynamical ones. By virtue of its nature of commonality, beyond-equilibrium thermodynamics should provide relationships between various static and dynamic material properties on the macroscopic or any other coarse-grained level of description. When statistical mechanics comes into the game, beyond-equilibrium thermodynamics may be regarded as the *theory of coarse-graining*: it should provide the structure of the equations for describing coarse-grained systems, and statistical mechanics should provide microscopic interpretations and expressions for the inputs of the phenomenological thermodynamic approach, so that the "macroscopic postulates are precisely and clearly the theorems of statistical mechanics." The reader should verify that the GENERIC approach used in this book for presenting a unified view of beyond-equilibrium thermodynamics fulfills all these requirements.

## A.2 EQUILIBRIUM STATES

A very fundamental notion in thermodynamics is the *state* concept. The state of an isolated thermodynamic system is described by a finite set of *state variables* ( $X_i$ ). Citing Callen,

Systems tend to subside to very simple states, independent of their specific history. ... *in all systems there is a tendency to evolve toward states in which the properties are determined by intrinsic factors and not by previously applied external influences. Such simple terminal states are, by definition, time independent. They are called equilibrium states.* [p. 13]

Next, the *internal energy*  $U$  needs to be established as a state variable. Callen introduces it as a macroscopic manifestation of definite conservation principles of

energy and summarizes the fundamental properties of equilibrium states in his first postulate:

**Postulate I.** *There exist particular states (called equilibrium states) that, macroscopically, are characterized completely by the specification of the internal energy  $U$  and a set of parameters  $X_1, X_2, \dots, X_t$  later to be specifically enumerated.* [p. 283]

In many applications of thermodynamics, the parameters or state variables  $X_i$  are the volume  $V$  and the mole numbers  $N_1, N_2, \dots, N_r$  of the chemically pure components of which a system is a mixture. These parameters, with the property that their value in a composite system is the sum of their values in each of the subsystems, are called *extensive*. In general, “the choice of variables in terms of which a given problem is formulated, while a seemingly innocuous step, is often the most crucial step in the solution” [p. 465]. If the choice of variables is so crucial, how can we understand which variables are relevant to describing the time independent states of a system? Callen demonstrates in the final part of his book on fundamentals that, for equilibrium systems, the answer to this question is intimately related to the *symmetries of the laws of nature*.

The conserved quantities are clearly the most natural variables to describe time independent states. According to Noether’s theorem, such conserved quantities result from the continuous symmetries of the dynamical behavior of a system. For example, symmetry under time translation implies the conservation of energy, and the conservation of electric charge is a consequence of the gauge symmetry of Maxwell’s equations. Another possible reason for variables to become relevant to the description of time independent states lies in the observation that certain dynamic modes in the limit of long wavelengths acquire a vanishing frequency.

An important general consequence of broken symmetry is formulated in the Goldstone theorem. It asserts that *any system with broken symmetry (and with certain weak restrictions on the atomic interactions) has a spectrum of excitations for which the frequency approaches zero as the wavelength becomes infinitely large.* [p. 464]

For a crystalline solid, for example, there exist infinitely many equally possible positions, slightly displaced by an arbitrary fraction of a lattice constant, which are related through the broken symmetry of translations. The fact that these positions are equally possible leads to a zero-frequency mode and to the occurrence of the volume as a state variable.

To return to the general formalism, we thus recognize that *all symmetries* [leading to conservation laws and Goldstone excitations] *must be taken into account in specifying the relevant state space of a system.* [p. 471]

These symmetry considerations are limited to equilibrium thermodynamics. In complex fluids, the choice of the relevant state variables will be more complicated. In fact, a fundamental challenge in applying beyond-equilibrium thermodynamics is to identify in some way the structural state variables  $X_i$  for a particular (class of) system(s). The relevant variables correspond to the slowest modes of a system. In

beyond-equilibrium thermodynamics, one thus needs to separate the slow and the fast variables and, after keeping only the slow as the relevant variables, one expects corrections to be governed by the ratio of the associated time scales, whereas the theory of equilibrium states deals with the truly time independent variables associated with symmetries. In that sense, beyond-equilibrium thermodynamics has an intrinsically approximate character absent in its equilibrium counterpart.

Considerations of the state concept introduced in Postulate I in connection with various forms of energy exchange lead to the definition of heat and work, as well as a balance equation for the internal energy  $U$ :

$$dU = \delta Q + \delta W. \quad (\text{A.1})$$

The symbol  $\delta$  is used instead of  $d$  since  $\delta Q$  and  $\delta W$  are not differentials of state variables (that is, not differentials of functions of  $U, X_1, X_2, \dots, X_t$ ) but are small amounts of heat and work. In Callen's words [p. 20], "Heat, like work, is only a form of energy *transfer* ... the energy  $U$  of a state *cannot* be considered as the sum of 'work' and 'heat' components." In general,  $\delta Q$  and  $\delta W$  are process-dependent quantities, and there are no corresponding state variables in the sense defined above. Equation (A.1) can be considered as a formal representation of the balance equation of internal energy derived from phenomenological considerations.

The use of the notions of *thermodynamic systems* and *equilibrium states* in this section deserves a few words of explanation. A thermodynamic system should actually be *defined* through a set of state variables and the accessible domain in the corresponding state space. Although one can formally define equilibrium states as time independent states of isolated systems, this definition is not very helpful for practical purposes because very long time scales might occur. For practical purposes, Callen hence proposes a rather indirect, somewhat provocative operational explanation [p. 15]: "In practice the criterion for equilibrium is circular. *Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory!*"

### A.3 BASIC PROBLEM OF THERMODYNAMICS

To keep a system in an equilibrium state, *constraints* are needed. If some of these constraints are released, the system will evolve to other states. What occurs then is, in fact, what Callen calls *the basic problem of thermodynamics*:

*The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system. [p. 26]*

It should be noted that Callen uses the term *closed* for systems that we nowadays usually refer to as *isolated*. The solution of the basic problem of thermodynamics is achieved through the entropy postulates, which "are, in fact, the most natural guess that we might make, providing the *simplest conceivable formal solution* to the basic

problem . . . the most economical form for the equilibrium criterion would be in terms of an extremum principle":

**Postulate II.** *There exists a function (called the entropy) of the extensive parameters, defined for all equilibrium states, and having the following property. The values assumed by the extensive parameters in the absence of a constraint are those that maximize the entropy over the manifold of constrained equilibrium states.* [p. 284]

**Postulate III.** *The entropy of a composite system is additive over the constituent subsystems (whence the entropy of each constituent system is a homogeneous first-order function of the extensive parameters). The entropy is continuous and differentiable and is a monotonically increasing function of the energy.* [p. 284]

**Postulate IV.** *The entropy of any system vanishes in the state for which  $T \equiv (\partial U / \partial S)_{X_1, X_2, \dots} = 0$ .* [p. 284]

The function introduced in Postulate II is called a *fundamental equation* of the system:

$$S = S(U, X_1, X_2, \dots, X_t). \quad (\text{A.2})$$

This is the entropy representation. By solving with respect to  $U$ —this is possible in view of the last part of Postulate III—one obtains the energy representation

$$U = U(S, X_1, X_2, \dots, X_t). \quad (\text{A.3})$$

Fundamental equations in thermodynamics deserve their name because they contain the information about all thermodynamic properties (equations of state, heat capacities, compressibilities, expansion coefficients, phase behavior, etc.) of the system. This, however, is primarily of theoretical interest, because for most systems no analytical expressions of the fundamental equations are available. The mere existence of fundamental equations, however, is already very important to establish relationships between various thermodynamic properties; this emphasis on relationships is the essence of thermodynamics.

The total differential of equation (A.3) is

$$dU = TdS + P_1dX_1 + P_2dX_2 + \dots P_t dX_t, \quad (\text{A.4})$$

with the temperature

$$T = \left( \frac{\partial U}{\partial S} \right)_{X_1, X_2, \dots, X_t} = T(S, X_1, X_2, \dots, X_t), \quad (\text{A.5})$$

and the thermodynamic forces

$$P_i = \left( \frac{\partial U}{\partial X_i} \right)_{S, X_1, X_2, \dots, X_{i-1}, X_{i+1}, \dots, X_t} = P_i(S, X_1, X_2, \dots, X_t). \quad (\text{A.6})$$

The functional dependencies implied by (A.5) and (A.6) are constitutive equations, known as *thermodynamic equations of state*. Contrary to fundamental equations like

(A.3), an equation of state does not contain the full information about the thermodynamic properties of the system but only part of it.

It should be emphasized that, despite the formal similarity of (A.1) and (A.4), these expressions are fundamentally different. Equation (A.1) is a balance equation for  $U$ , expressed in *process-dependent* quantities, describing an energy transfer, whereas (A.4) is the total differential of the dependent state variable  $U$ , expressed as a function of a complete set of state variables.

It should also be noted that, in the treatment of Callen, at this point it is not evident that  $T$  is in fact the usual temperature and how the  $P_i$  are related to the usual mechanical variables, such as pressure. This, in fact, turns out to be a consequence of the entropy maximum principle, expressed in Callen's second postulate. By considering the equilibrium of a system with external reservoirs, it follows that in sufficiently slow, *quasi-static* processes

$$\delta Q = TdS, \quad (\text{A.7})$$

and

$$P_i = P_i^e, \quad (\text{A.8})$$

where  $-P_i$  is a thermodynamic force (such as the thermodynamic pressure) and  $-P_i^e$  the corresponding external, mechanical force (such as the mechanical pressure). *Quasi-static* processes play an important role in the determination of thermodynamic quantities. These processes may be considered as trajectories in the manifold of equilibrium states. It should be noted, however, that quasi-static processes are an idealization because real processes always involve nonequilibrium intermediate states.

As mentioned above, the variables  $U$ ,  $S$  and  $X_1 \dots X_t$  are extensive, that is, proportional to the size of the system. As a consequence, (A.3) is homogeneous of the first order:

$$U(\lambda S, \lambda X_1, \lambda X_2, \dots, \lambda X_t) = \lambda U(S, X_1, X_2, \dots, X_t). \quad (\text{A.9})$$

By differentiating (A.9) with respect to  $\lambda$  and setting  $\lambda$  equal to unity, one can derive the *Euler equation*,

$$U = TS + \sum_{i=1}^t P_i X_i, \quad (\text{A.10})$$

and the so-called *Gibbs-Duhem equation*,

$$SdT + \sum_{i=1}^t X_i dP_i = 0. \quad (\text{A.11})$$

Note, however, that in the modeling of complex fluids in general not all of the structural variables will be extensive. Structural parameters, like configuration tensors etc., which describe the internal state of a system, are an example of this. In such cases, one cannot directly generalize the expressions (A.10) and (A.11).

A classical example in thermodynamics is a system of  $N$  moles of a gas or liquid in a volume  $V$ . In this case, the total differential (A.4) of  $U = U(S, V, N)$  becomes

$$dU = TdS - PdV + \mu dN, \quad (\text{A.12})$$



where  $P$  is the thermodynamic pressure and  $\mu$  is the chemical potential. The Gibbs-Duhem relation (A.11) becomes

$$SdT - VdP + Nd\mu = 0, \quad (\text{A.13})$$

probably better known in the molar form

$$d\mu = -\tilde{s}dT + \tilde{v}dP, \quad (\text{A.14})$$

with  $\tilde{s} = S/N$  and  $\tilde{v} = V/N$ .

## A.4 THERMODYNAMIC POTENTIALS

Equations (A.2) and (A.3) are probably the most fundamental but certainly not the most practical equations of thermodynamics. The reason is that, in many situations, the variables used in these expressions are not the ones controlled or measured in practice. Processes with temperature and pressure control are for instance more common than processes with controlled entropy and volume. Fortunately, there exist transformations by which fundamental equations can be transformed with conservation of their fundamental nature, that is, the property that they contain all information about the thermodynamic properties of the system. These transformations are the so-called *Legendre transformations*, and the new functions, which are the result of the transformation, are called thermodynamic potentials. By means of Legendre transformations, all extensive and intensive state variables ( $U, S, X_1, \dots, X_t, T, P_1, \dots, P_t$ ) are elevated to an equal footing.

The relevance of these transformations in thermodynamics should not be underestimated. To cite Callen:

Multiple equivalent formulations also appear in Mechanics—Newtonian, Lagrangian, and Hamiltonian formulations are tautologically equivalent. Again certain problems are more tractable in a Lagrangian formalism than in a Newtonian formalism, or vice versa. But the difference in convenience of the different formalisms is enormously greater in thermodynamics. It is for this reason that *the general theory of transformations among equivalent representations is here incorporated as a fundamental aspect of thermostatistical theory.* [p. 131]

A partial Legendre transformation can be made by replacing the variables  $X_0, X_1, \dots, X_s$  by  $P_0, P_1, \dots, P_s$  (where  $s < t$ ,  $X_0 = S$ ,  $P_0 = T$ , and the first  $s$  variables, instead of any  $s$  variables, are selected without loss of generality). The Legendre transformed function is

$$U[P_0, P_1, \dots, P_s] = U - \sum_{i=0}^s P_i X_i. \quad (\text{A.15})$$

Following Callen, we here employ the notation  $U[P_0, P_1, \dots, P_s]$  to denote the function obtained by making a Legendre transformation with respect to  $X_0, X_1, \dots, X_s$

on the function  $U(X_1, X_2, \dots, X_t)$ . Thus  $U[P_0, P_1, \dots, P_s]$  is a function of the independent variables  $P_0, P_1, \dots, P_s, X_{s+1}, X_{s+2}, \dots, X_t$ . The natural derivatives of this function are

$$\frac{\partial U[P_0, P_1, \dots, P_s]}{\partial P_k} = -X_k \quad (k = 0, 1, \dots, s) \quad (\text{A.16})$$

$$\frac{\partial U[P_0, P_1, \dots, P_s]}{\partial X_k} = P_k \quad (k = s+1, s+2, \dots, t) \quad (\text{A.17})$$

and consequently

$$dU[P_0, P_1, \dots, P_s] = \sum_{i=0}^s (-X_i) dP_i + \sum_{i=s+1}^t P_i dX_i. \quad (\text{A.18})$$

For the example of a gas or a fluid, the following well-known thermodynamic potentials are obtained by Legendre transformation: *the Helmholtz potential* or *Helmholtz free energy*,

$$F = U[T] = U - TS, \quad (\text{A.19})$$

*the enthalpy*,

$$H = U[P] = U + PV, \quad (\text{A.20})$$

and *the Gibbs potential* or *Gibbs free energy*,

$$G = U[T, P] = U - TS + PV. \quad (\text{A.21})$$

The fundamental equations of these functions in differential form read:

$$\begin{aligned} dF &= -SdT - PdV + \mu dN, \\ dH &= TdS + VdP + \mu dN, \\ dG &= -SdT + VdP + \mu dN. \end{aligned} \quad (\text{A.22})$$

The coefficients in these expressions are functions of the corresponding variables. In this way, a set of equations of state is associated with each of the potentials, for example

$$\begin{aligned} S(T, V, N) &= -\left(\frac{\partial F}{\partial T}\right)_{V, N}, \\ P(T, V, N) &= -\left(\frac{\partial F}{\partial V}\right)_{T, N}, \\ \mu(T, V, N) &= \left(\frac{\partial F}{\partial N}\right)_{T, V}, \end{aligned} \quad (\text{A.23})$$

and so on.

For the Helmholtz potential function  $F(T, V, N)$  an extremum principle similar to Callen's Postulate II applies. This result, which can be derived from Postulate II by

considering a small system in thermal contact with a large reservoir of temperature  $T^r$ , reads:

**Helmholtz Potential Minimum Principle.** *The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential over the manifold of states for which  $T = T^r$ .* [p. 155]

Similar results may be derived for the other thermodynamic potentials.

There exists an alternative to thermodynamic potentials to condense all the information about a thermodynamic system into a single function that is useful in the context of developing beyond-equilibrium thermodynamics:

Whereas the most common functions definable in terms of Legendre transformations are those mentioned ... [above], another set can be defined by performing the Legendre transformation on the entropy rather than on the energy. That is, the fundamental relation in the form  $S = S(U, V, N_1, N_2, \dots)$  can be taken as the relation on which the transformation is performed. Such Legendre transforms of the entropy were invented by Massieu in 1869 and actually predated the transforms of the energy introduced by Gibbs in 1875. We refer to the transforms of the entropy as *Massieu functions*, as distinguished from the *thermodynamic potentials* transformed from the energy. The Massieu functions will turn out to be particularly useful in the theory of irreversible thermodynamics, and they also arise naturally in statistical mechanics and in the theory of thermal fluctuations. [p. 151]

## A.5 MAXWELL RELATIONS AND STABILITY CRITERIA

The material quantities that are of primary interest in applications to thermodynamics are the equations of state, like (A.23), and in particular derivatives such as  $(\frac{\partial S}{\partial T})_{V,N}$ . It should be noted that, because the equations of state are obtained by differentiation of fundamental equations, these quantities are second derivatives of a thermodynamic potential. By using the rule of interchanging the order of partial differentiation, one readily obtains the so-called *Maxwell relations*. For example, one has

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \quad (\text{A.24})$$

and hence

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N}. \quad (\text{A.25})$$

These interrelations are heavily used in thermodynamic calculations. Maxwell, whose turn of mind was geometrical, obtained (A.25), and similar relations, from the properties of a parallelogram; he concluded that such a relation “is a merely geometrical truth, and does not depend upon thermodynamic principles,” whereas he offered the formulation in the language of differential calculus only as a footnote.<sup>5</sup>

<sup>5</sup> See p. 169 of Maxwell, *Theory of Heat* (Dover, 2001).

Besides derivatives of the equations of state, one also encounters derivatives like  $(\frac{\partial S}{\partial V})_{P,T}$ ,  $(\frac{\partial U}{\partial P})_{G,N}$ , and so on. In simple cases, a reduction of quantities of this type to more familiar expressions is possible by the use of some identities of calculus. Callen describes a general procedure in five steps for the reduction of derivatives by using such identities and the Maxwell relations [p. 186–189]. In addition, a more general method based on Jacobian representations of partial derivatives is available.

The second derivatives of the thermodynamic potentials are not only the basis for the Maxwell relations; they are also fundamental in considerations about thermodynamic stability. The starting point is, again, the maximum entropy postulate. A consequence of this postulate is that the hypersurface  $S = S(U, X_1, \dots, X_t)$  in the thermodynamic configuration space should have the property that it lies everywhere below its tangent planes. This implies conditions for the derivatives of the fundamental relation. For example, in the case  $S = S(U, V, N)$ , we have

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N} \leq 0, \quad (\text{A.26})$$

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_{U,N} \leq 0, \quad (\text{A.27})$$

and

$$\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0. \quad (\text{A.28})$$

The positiveness of physical quantities like specific heats, compressibilities, and expansion coefficients is a direct consequence of these thermodynamic stability requirements. Chemical equilibria for systems consisting of several components can be treated accordingly.

If criteria of stability are not satisfied, a system breaks up into two or more phases. The molar Gibbs potential of each component is then equal in each phase. The dimension  $\bar{f}$  of the thermodynamic space in which a given number  $M$  of phases can exist for a system of  $r$  components is given by the *Gibbs phase rule*

$$\bar{f} = r - M + 2. \quad (\text{A.29})$$

## A.6 STATISTICAL MECHANICS

All the thermodynamic properties of a system are determined by a single fundamental equation, and equilibrium thermodynamics implies very general relationships between the various thermodynamic properties. To understand a particular system, however, we are still faced with the problem of determining an appropriate fundamental equation. One option would be to collect experimental information about various equations of state, which could then be used to construct a fundamental equation. Another option would be to calculate a fundamental equation from an atomistic understanding of the system by means of statistical mechanics. The key to this route to

fundamental equations is a microscopic understanding of the concept of entropy. In Callen's words,

... the entropy is one of a set of extensive parameters, together with the energy, volume, mole numbers and magnetic moment. As these latter quantities each have clear and fundamental physical interpretations it would be strange if the entropy alone were to be exempt from physical interpretation.

The subject of statistical mechanics provides the physical interpretation of the entropy, and it accordingly provides a heuristic justification for the extremum principle of thermodynamics. [p. 329]

The basis of statistical mechanics can actually be established in a few lines, provided that one formulates one more postulate, the *fundamental postulate of statistical mechanics*:

The assumption of equal probability of all permissible microstates is the fundamental postulate of statistical mechanics [a permissible microstate being one consistent with the external constraints] ....

Suppose now that some external constraint is removed—such as the opening of a valve permitting the system to expand into a larger volume. From the microphysical point of view the removal of the constraint activates the possibility of many microstates that previously had been precluded. Transitions occur into these newly available states. After some time the system will have lost all distinction between the original and the newly available states, and the system will thenceforth make random transitions that sample the *augmented* set of states with equal probability. *The number of microstates among which the system undergoes transitions, and which thereby share uniform probability of occupation, increases to the maximum permitted by the imposed constraints.*

This statement is strikingly reminiscent of the entropy postulate of thermodynamics, according to which the entropy increases to the maximum permitted by the imposed constraints. It suggests that the entropy can be identified with the number of microstates consistent with the imposed macroscopic constraints.

One difficulty arises: The entropy is additive (extensive), whereas the number of microstates is multiplicative. The number of microstates available to two systems is the *product* of the numbers available to each (...). To interpret the entropy, then, we require an *additive* quantity that measures the number of microstates available to a system. The (unique!) answer is to *identify the entropy with the logarithm of the number of available microstates* (the logarithm of a product being the sum of the logarithms). Thus

$$S = k_B \ln \Omega$$

where  $\Omega$  is the number of microstates consistent with the macroscopic constraints. The constant prefactor merely determines the scale of  $S$ ; it is chosen to obtain agreement with the Kelvin scale of temperature ...

... this single postulate is dramatic in its brevity, simplicity, and completeness. The statistical mechanical formalism that derives directly from it is one in which we 'simply' calculate the logarithm of the number of states available to the system, thereby obtaining  $S$  as a function of the constraints  $U$ ,  $V$ , and  $N$ . That is, it is statistical mechanics in the entropy formulation, or, in the parlance of the field, it is statistical mechanics in the *microcanonical formalism*. [p. 331–332]

The fundamental postulate of statistical mechanics can be supported by symmetry arguments. Following Callen, for any two states  $i$  and  $j$ , “the interchangeability of future and past, or the time reversibility of physical laws, associates the transitions  $i \rightarrow j$  and  $j \rightarrow i$  and leads directly to the equality . . . of the transition probabilities” [p. 468]. This principle of detailed balance leads to the principle of equal probabilities of states in the microcanonical ensemble, so that “*the equal probabilities of permissible states for a closed system in equilibrium is a consequence of time reversal symmetry of the relevant quantum mechanical laws*” [p. 468]. Again, symmetry plays an important role for a fundamental understanding of principles. Ergodic theory offers an alternative approach to justify the fundamental postulate of statistical mechanics.

According to the well-established microcanonical formalism, the calculation of the fundamental equation for the entropy amounts to counting the number of microstates for given extensive variables (more precisely, one needs to consider intervals around a given energy to find any states with the prescribed energy, where the entropy is essentially independent of the size of the interval). Whereas the microcanonical formalism solves the fundamental problem of statistical mechanics, it may be very useful for practical purposes to work in other formalisms, in particular, in the so-called *canonical formalism*:

As in thermodynamics, the entropy representation is not always the most convenient representation. For statistical mechanical calculations it is frequently so inconvenient that it is analytically intractable. [p. 332]

The canonical formalism can be derived by considering the system of interest in contact with a thermal reservoir of a given temperature rather than an isolated system. The “system plus the reservoir constitute a *closed system*, to which the principle of equal probability of microstates again applies” [p. 349]. For the system alone, however, microstates then do not have the same probability. Rather, the probabilities are proportional to the Boltzmann factors, and the normalization factor for the probabilities is given by the *canonical partition function*,  $Z$ , as a function of the temperature and the extensive mechanical state variables. The Helmholtz free energy is given by the famous relation

$$F = -k_B T \ln Z = -k_B T \ln \sum_j e^{-E_j/(k_B T)}, \quad (\text{A.30})$$

“which should be committed to memory” [p. 351]. Equation (A.30) is the basis for most first-principles calculations of thermodynamic properties, in particular, by Monte Carlo methods.

In the canonical approach, the probabilities of all the microstates are known, so that not only averages but also fluctuations are accessible. One thus obtains the *theory of fluctuations* which establishes a close relationship between thermodynamic material properties and the magnitude of fluctuations (both are given by the second-order derivatives of thermodynamic potentials).

Callen’s approach to statistical mechanics is actually based on quantum systems, for which we have a discrete set of microstates. The quantum approach has a number of advantages. The natural concept of indistinguishable particles avoids the classical

overestimate of the number of states leading to a nonextensive entropy (this problem is associated with the famous key words “Gibbs’ paradox” and “correct Boltzmann counting”). The existence of (weakly degenerate) ground states implies that the entropy goes to zero when the absolute temperature approaches zero. Finally, only by means of Planck’s constant can one naturally form the dimensionless quantities required for taking logarithms.

## A.7 PERSPECTIVES

Equilibrium thermodynamics is in perfect shape. The all-encompassing problem of equilibrium thermodynamics has been identified, a clearly structured elegant formalism has been developed within a postulational approach, the postulates can be supported by statistical mechanics, the universal features have been elaborated, successful sets of state variables have been identified and corroborated for many problems, the rules for atomistic calculations of fundamental equations have been discovered, transformations for simplifying practical calculations have been found, and an enormous number of problems in various fields of science and engineering have been solved. Beyond-equilibrium thermodynamics should now be shaped to a similar level of perfection.