Phenomenological thermodynamics in a nutshell

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Abstract. This paper gives a concise, mathematically rigorous description of phenomenological equilibrium thermodynamics for single-phase systems in the absence of chemical reactions and external forces.

The present approach is similar to that of CALLEN [9], who introduces in his well-known thermodynamics book the basic concepts by means of a few postulates from which everything else follows. His setting is modified to match the more fundamental approach based on statistical mechanics. Thermodynamic stability is derived from kinematical properties of states outside equilibrium by rigorous mathematical arguments, superseding Callen's informal arguments that depend on a dynamical assumption close to equilibrium.

From the formulas provided, it is an easy step to go to various examples and applications discussed in standard textbooks such as CALLEN [9] or REICHL [32]. A full discussion of global equilibrium would also involve the equilibrium treatment of multiple phases and chemical reactions. Since their discussion offers no new aspects compared with traditional textbook treatments, they are not treated here.

An older version of this document can be found as a chapter in the online book
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    Classical and Quantum Mechanics via Lie algebras,
    2011.
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Contents

1   Standard thermodynamical systems

This paper gives a concise, mathematically rigorous description of phenomenological equilibrium thermodynamics for single-phase systems in the absence of chemical reactions and external forces. We discuss only the special but very important case of thermodynamic systems describing the single-phase global equilibrium of matter composed of one or several kinds of pure substances in the absence of chemical reactions and external forces. We call such systems **standard thermodynamic systems**; they are ubiquitous in the applications. In particular, a standard system is considered to be uncharged, homogeneous, and isotropic, so that each finite region looks like any other and is very large in microscopic units.

Pure substances of fixed chemical composition are labeled by an index j. Composite substances, called **mixtures**, are composed of several pure substances called **components**. Each component has an index j; we denote by J the set of all these indices. A standard thermodynamic system is completely characterized by[1] the **mole number** n_j of each component j, the corresponding **chemical potential** μ_j of component j, the **volume** V, the **pressure** P, the **temperature** T, the **entropy** S, and the **internal energy** U. These variables, the **extensive** variables n_j, V, S, U and the **intensive** variables μ_j, P, T, are jointly called the **basic thermodynamic variables**; they take real numbers as values. (In this

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[1]In the terminology, we mainly follow the IUPAC convention (ALBERTY [2, Section 7]). For a history of thermodynamics notation, see BATTINO et al. [7].

paper, all numbers are real.) We group the n_j and the μ_j into vectors n and μ indexed by J and write $\mu \cdot n = \sum_{j \in J} \mu_j n_j$. In the special case of a **pure substance**, there is just a single component; then we drop the indices and have $\mu \cdot n = \mu n$.

Equilibrium thermodynamics is about characterizing so-called equilibrium states in terms of intensive and extensive variables and their relations, and comparing them with similar nonequilibrium states. In a nonequilibrium state, only extensive variables have a well-defined meaning; but these are not sufficient to characterize system behavior completely.

All valid statements in the equilibrium thermodynamics of standard systems can be deduced from the following definition. In this paper we take the properties asserted in the definition as axioms. However, they can in turn be deduced from appropriate microscopic assumptions using statistical mechanics; for example, convexity is a consequence of the statistical fact that covariance matrices are positive semidefinite.

1.1 Definition. (Phenomenological thermodynamics)
(i) Temperature T and volume V are positive, entropy S and mole numbers n_j are nonnegative. The **extensive variables** U, S, V, n_j are additive under the composition of disjoint subsystems. We combine the n_j into a column vector with these components.

(ii) The **intensive variables** T, P, μ are related by the **equation of state**

$$\Delta(T, P, \mu) = 0. \tag{1}$$

The **system function** Δ appearing in the equation of state is jointly convex[2] in T, P, μ. (It will follow from Theorem 1.2(iii) that Δ is also monotone increasing in T and each μ_i, and monotone decreasing in P.) The set of (T, P, μ) satisfying $T > 0$ and the equation of state is called the **state space**.[3]

(iii) The internal energy U satisfies the **Euler inequality**

$$U \geq TS - PV + \mu \cdot n \tag{2}$$

for all (T, P, μ) in the state space.

(iv) **Equilibrium states** have well-defined intensive and extensive variables satisfying equality in (2). A system is in **equilibrium** if it is completely characterized by an equilibrium state.

This is the complete list of assumptions defining phenomenological equilibrium thermodynamics for standard systems; the system function Δ can be determined either by fitting to experimental data, or by calculation from a more fundamental description, namely the grand canonical partition function of statistical mechanics.

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[2]see Appendix A
[3]Typically, the pressure P is also positive. However, for solids, equilibrium states with $P < 0$ are possible when exposed to tensile forces.

All other properties follow from the system function. Thus, all equilibrium properties of a material are characterized by the system function Δ. (In contrast, nonequilibrium properties depend on additional dynamical assumptions, which, except close to equilibrium, vary among the various scientific schools. We will discuss nonequilibrium properties only in passing.)

Surfaces where the system function is not differentiable correspond to so-called **phase transitions**. The equation of state shows that, apart from possible phase transitions, the state space has the structure of an $(s-1)$-dimensional manifold in $\mathbb{R}^s$, where s is the number of intensive variables; in case of a standard system, the manifold dimension is therefore one higher than the number of components.

Standard systems describe only a single phase of a substance (typically the solid, liquid, or gas phase), and changes between these as some thermodynamic variable(s) change. Thermodynamic systems with multiple phases (e.g., boiling water, or water containing ice cubes) are only piecewise homogeneous. Each phase may be described separately as a standard thermodynamic system. But discussing the equilibrium at the interfaces between different phases needs some additional effort. (This is described in all common textbooks on thermodynamics.) Therefore, we consider only regions of the state space where the system function Δ is twice continuously differentiable.

Each equilibrium instance of the material is characterized by a particular state (T, P, μ), from which all equilibrium properties can be computed:

1.2 Theorem.
(i) In any equilibrium state, the extensive variables are given by

$$S = \Omega \frac{\partial \Delta}{\partial T}(T, P, \mu), \quad V = -\Omega \frac{\partial \Delta}{\partial P}(T, P, \mu), \quad n = \Omega \frac{\partial \Delta}{\partial \mu}(T, P, \mu), \tag{3}$$

*and the **Euler equation***

$$U = TS - PV + \mu \cdot n, \tag{4}$$

*the case of equality in (2). Here Ω is a positive number independent of T, P, and μ, called the **system size**.*

(ii) In equilibrium, the matrix

$$\Sigma := \begin{pmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial S}{\partial P} & \dfrac{\partial S}{\partial \mu} \\[1em] -\dfrac{\partial V}{\partial T} & -\dfrac{\partial V}{\partial P} & -\dfrac{\partial V}{\partial \mu} \\[1em] \dfrac{\partial n}{\partial T} & \dfrac{\partial n}{\partial P} & \dfrac{\partial n}{\partial \mu} \end{pmatrix} \tag{5}$$

*is symmetric and positive semidefinite. In particular, we have the **Maxwell reciprocity relations***

$$-\frac{\partial V}{\partial T} = \frac{\partial S}{\partial P}, \quad \frac{\partial n_j}{\partial T} = \frac{\partial S}{\partial \mu_j}, \quad \frac{\partial n_j}{\partial P} = -\frac{\partial V}{\partial \mu_j}, \quad \frac{\partial n_j}{\partial \mu_k} = \frac{\partial n_k}{\partial \mu_j} \tag{6}$$

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and the **stability conditions**

$$\frac{\partial S}{\partial T} \geq 0, \quad \frac{\partial V}{\partial P} \leq 0, \quad \frac{\partial n_j}{\partial \mu_j} \geq 0. \tag{7}$$

(iii) $\Delta(T, P, \mu)$ is monotone increasing in T and each μ_i, and strictly decreasing in P.

Proof. At fixed S, V, n, the inequality (2) holds in equilibrium with equality, by definition. Therefore the triple (T, P, μ) is a maximizer of $TS - PV + \mu \cdot n$ under the constraints $\Delta(T, P, \mu) = 0$, $T > 0$. A necessary condition for a maximizer is the stationarity of the Lagrangian

$$L(T, P, \mu) = TS - PV + \mu \cdot n - \Omega \Delta(T, P, \mu)$$

for some Lagrange multiplier Ω. Setting the partial derivatives to zero gives (3), and since the maximum is attained in equilibrium, the Euler equation (4) follows. The system size Ω is positive since $V > 0$ and Δ is decreasing in P. The symmetry of the Hessian matrix

$$\Delta''(T, P, \mu) = \begin{pmatrix} \dfrac{\partial^2 \Delta}{\partial T^2} & \dfrac{\partial^2 \Delta}{\partial P \partial T} & \dfrac{\partial^2 \Delta}{\partial \mu \partial T} \\[2mm] \dfrac{\partial^2 \Delta}{\partial T \partial P} & \dfrac{\partial^2 \Delta}{\partial P^2} & \dfrac{\partial^2 \Delta}{\partial \mu \partial P} \\[2mm] \dfrac{\partial^2 \Delta}{\partial T \partial \mu} & \dfrac{\partial^2 \Delta}{\partial P \partial \mu} & \dfrac{\partial^2 \Delta}{\partial \mu^2} \end{pmatrix} = \Omega^{-1} \begin{pmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial S}{\partial P} & \dfrac{\partial S}{\partial \mu} \\[2mm] -\dfrac{\partial V}{\partial T} & -\dfrac{\partial V}{\partial P} & -\dfrac{\partial V}{\partial \mu} \\[2mm] \dfrac{\partial n}{\partial T} & \dfrac{\partial n}{\partial P} & \dfrac{\partial n}{\partial \mu} \end{pmatrix} = \Omega^{-1} \Sigma$$

of Δ implies the Maxwell reciprocity relations. Since Δ is convex, Σ is positive semidefinite; hence the diagonal elements of Σ are nonnegative, giving the stability conditions. Finally, (3) implies that Δ is monotone increasing in T and each μ_j since $S, n_j \geq 0$, and strictly decreasing in P since $V > 0$. $\square$

Many entries of the matrix Σ from (5) are observable **response functions**. Note that not only the diagonal elements but the determinants of *all* principal submatrices of Σ must be nonnegative. This gives further stability conditions.

Let μ_U and μ_S be constant vectors indexed by J. Then replacing μ, U, S, and Δ by

$$\mu' := \mu + \mu_U + T\mu_S, \quad U' := U + \mu_U \cdot n, \quad S' := S - \mu_S \cdot n,$$

$$\Delta'(T, P, \mu) := \Delta(T, P, \mu - \mu_U - T\mu_S)$$

preserves (3) and (4), and hence all equilibrium properties. The existence of these **gauge transformations** implies that the chemical potentials are determined only up to a substance-dependent shift linear in the temperature, and the internal energy and entropy are only determined up to an arbitrary linear combinations of the mole numbers. This is an instance of the deeper problem to determine under which conditions thermodynamic variables are controllable.

1.3 Example. The equilibrium behavior of electrically neutral gases at sufficiently low pressure can be modelled as ideal gases. An **ideal gas** is defined by a system function of the form

$$\Delta(T, P, \mu) = \sum_{j \in J} P_j(T) e^{\mu_j/RT} - P, \tag{8}$$

where the $P_j(T)$ are positive functions of the temperature,

$$R \approx 8.31446 \, JK^{-1}\mathrm{mol}^{-1} \tag{9}$$

is the **universal gas constant**[4], and we use the bracketing convention $\mu_j/RT = \mu_j/(RT)$. Differentiation with respect to P shows that $\Omega = V$ is the system size, and from (1), (3), and (4), we find that, in equilibrium,

$$P = \sum_j P_j(T) e^{\mu_j/RT}, \quad S = V \sum_j \Big(\frac{\partial}{\partial T} P_j(T) - \frac{\mu_j P_j(T)}{RT^2} \Big) e^{\mu_j/RT},$$

$$n_j = \frac{P_j(T)V}{RT} e^{\mu_j/RT}, \quad U = V \sum_j \Big(T \frac{\partial}{\partial T} P_j(T) - P_j(T) \Big) e^{\mu_j/RT}.$$

Expressed in terms of T, V, n, we have

$$PV = RT \sum_j n_j, \quad \mu_j = RT \log \frac{RT n_j}{P_j(T)V}, \quad U = \sum_j u_j(T) n_j,$$

where, with $P - j'(T) = dP_j(T)/dT$,

$$u_j(T) = RT \Big(\frac{T P_j'(T)}{P_j(T)} - 1 \Big), \tag{10}$$

from which S can be computed by means of the Euler equation (4). In particular, for one **mole** of a pure substance, defined by $n = 1$, we get the **ideal gas law**

$$PV = RT \tag{11}$$

discovered by CLAPEYRON [13]; cf. JENSEN [21].

In general, the difference $u_j(T) - u_j(T')$ can be found experimentally by measuring the energy needed for raising or lowering the temperature of a component j from T' to T while keeping the n_j constant. In terms of infinitesimal increments, expressed through the **heat capacities**

$$C_j(T) = du_j(T)/dT,$$

we have

$$u_j(T) = u_j(T') + \int_{T'}^{T} dT \, C_j(T).$$

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[4]For the internationally recommended values of this and other constants, their accuracy, determination, and history, see MOHR et al. [28].

From the definition (10) of $u_j(T)$, we find that

$$P_j(T) = P_j(T') \exp \int_{T'}^{T} \frac{dT}{T} \Big(1 + \frac{u_j(T)}{RT} \Big).$$

Thus there are two undetermined integration constants for each component. In view of the gauge transformations mentioned above, these can be chosen arbitrarily without changing the empirical content. The gauge transformation for Δ implies that $P_j(T)$ and $u_j(T)$ should be replaced by

$$P_j'(T) := e^{-(\mu_{Uj} + T\mu_{Sj})/RT} P_j(T), \quad u_j'(T) := u_j(T) + \mu_{Uj}.$$

Therefore the partial pressures $P_j(T)e^{\mu_j/RT}$ are unaffected by the gauge transformation and hence observable. For an ideal gas, the gauge freedom can be fixed by choosing a particular **standard temperature** T_0 and setting arbitrarily $u_j(T_0) = 0$, $\mu_j(T_0) = 0$. Alternatively, at sufficiently large temperature T, heat capacities are usually nearly constant, and making use of the gauge freedom, we may simply assume that

$$u_j(T) = h_{j0}T, \quad P_j(T) = P_{j0}T \quad \text{for large } T.$$

2 The laws of thermodynamics

In global equilibrium, all thermal variables are constant[5] throughout the system, except at phase boundaries, where the extensive variables may exhibit jumps and only the intensive variables remain constant. This is sometimes referred to as the **zeroth law of thermodynamics** (FOWLER & GUGGENHEIM [17]) and characterizes global equilibrium; it allows one to measure intensive variables (like temperature) by bringing a calibrated instrument that is sensitive to this variable (for temperature a thermometer) into equilibrium with the system to be measured.

For example, the ideal gas law (11) can be used as a basis for the construction of a **gas thermometer**: The amount of expansion of volume in a long, thin tube can easily be read off from a scale along the tube. We have $V = aL$, where a is the cross section area and L is the length of the filled part of the tube, hence $T = (aP/R)L$. Thus, at constant pressure, the temperature of the gas is proportional to L. For the history of temperature, see ROLLER [36] and TRUESDELL [39].

We say that two thermodynamic systems are brought in good **thermal contact** if, after a short time, the joint system tends to an equilibrium state. To measure the temperature of a system, one brings it in thermal contact with a thermometer and waits until equilibrium is established. The system and the thermometer will then have the same temperature, which can be read off from the thermometer. If the system is much larger than the thermometer,

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[5]This assumes the absence of external fields. An ideal gas in a constant gravitational field has a spatially nonuniform density. From the present point of view, this situation (as any other involving external fields) must be viewed as a system being in stationary local equilibrium, to be treated with nonequilibruim techniques.

this temperature will be essentially the same as the temperature of the system before the measurement. For a survey of the problems involved in defining and measuring temperature outside equilibrium, see CASAS-VÁSQUEZ & JOU [10].

To be able to formulate the first law of thermodynamics we need the concept of a reversible change of states, i.e., changes preserving the equilibrium condition. For use in later sections, we define the concept in a slightly more general form, writing α for P and μ jointly. We need to assume that the system under study is embedded into its environment in such a way that, at the boundary, certain thermodynamic variables are kept constant and independent of position. This determines the **boundary conditions** of the thermodynamic system; see the discussion in Section 3.

2.1 Definition. A **state variable** is an almost everywhere continuously differentiable function $\phi(T, \alpha)$ defined on the state space (but sometimes only on an open and dense subset of it). Temporal changes in a state variable that occur when the boundary conditions are kept fixed are called **spontaneous changes**. A **reversible transformation** is a continuously differentiable mapping

$$\lambda \to (T(\lambda), \alpha(\lambda))$$

from a real interval into the state space; thus $\Delta(T(\lambda), \alpha(\lambda)) = 0$. The **differential**[6]

$$d\phi = \frac{\partial \phi}{\partial T} dT + \frac{\partial \phi}{\partial \alpha} \cdot d\alpha, \tag{12}$$

obtained by multiplying the chain rule by $d\lambda$, describes the change of a state variable ϕ under arbitrary (infinitesimal) reversible transformations.

Reversible changes per se have nothing to do with changes in time. However, by sufficiently slow, quasistatic changes of the boundary conditions, reversible changes can often be realized approximately as temporal changes. The degree to which this is possible determines the efficiency of thermodynamic machines. The analysis of the efficiency by means of the so-called **Carnot cycle** was the historical origin of thermodynamics.

The state space is often parameterized by different sets of state variables, as required by the application. If $T = T(\kappa, \lambda)$, $\alpha = \alpha(\kappa, \lambda)$ is such a parameterization then the state variable $g(T, \alpha)$ can be written as a function of (κ, λ),

$$g(\kappa, \lambda) = g(T(\kappa, \lambda), \alpha(\kappa, \lambda)). \tag{13}$$

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[6]Informally, one may consider differentials as changes in states sufficiently small that a first order sensitivity analysis is appropriate: If x changes by a small amount dx then $y = f(x)$ changes by (approximately) the small amount $dy = f'(x)dx$, and analogous formulas hold in the multivariate case.

Another way to visualize equations or inequalities involving differentials is to view a reversible transformation as being realized (slowly but) continuously in time. Then the thermodynamic variables change continuously along a reversible path, and (as in the consideration of Carnot cycles) one can integrate the differentials along these paths, resulting in equations and inequalities of corresponding integrated quantities.

In formal mathematical terms, differentials are exact linear forms on the state space manifold; but we make no use of this.

This notation, while mathematically ambiguous, is common in the literature; the names of the argument decide which function is intended. When writing partial derivatives without arguments, this leads to serious ambiguities. These can be resolved by writing $\left(\frac{\partial g}{\partial \lambda}\right)_\kappa$ for the partial derivative of (13) with respect to λ; it can be evaluated using (12), giving the **chain rule**

$$\left(\frac{\partial g}{\partial \lambda}\right)_\kappa = \frac{\partial g}{\partial T}\left(\frac{\partial T}{\partial \lambda}\right)_\kappa + \frac{\partial g}{\partial \alpha} \cdot \left(\frac{\partial \alpha}{\partial \lambda}\right)_\kappa. \tag{14}$$

Here the partial derivatives in the original parameterization by the intensive variables are written without parentheses.

Differentiating the equation of state (1), using the chain rule (12), and simplifying using (3) gives the **Gibbs-Duhem equation**

$$0 = SdT - VdP + n \cdot d\mu \tag{15}$$

for reversible changes. If we differentiate the Euler equation (4), we obtain

$$dU = TdS + SdT - PdV - VdP + \mu \cdot dn + n \cdot d\mu,$$

and using (15), this simplifies to the **first law of thermodynamics**

$$dU = TdS - PdV + \mu \cdot dn. \tag{16}$$

Historically, the first law of thermodynamics took on this form only gradually, through work by MAYER [27], JOULE [23], HELMHOLTZ [20], and CLAUSIUS [14].

Considering global equilibrium from a fundamental point of view, the extensive variables are the variables that are conserved, or at least change so slowly that they may be regarded as time independent on the time scale of interest. In the absence of chemical reactions, the mole numbers, the entropy, and the internal energy are conserved; the volume is a system size variable which, in the fundamental view, must be taken as infinite (thermodynamic limit) to exclude the unavoidable interaction with the environment.

However, real systems are always in contact with their environment, and the conservation laws are approximate only. In thermodynamics, the description of the system boundary is generally reduced to the degrees of freedom observable at a given resolution. The result of this reduced description (for derivations, see, e.g., BALIAN [6], GRABERT [19], RAU & MÜLLER [31]) is a dynamical effect called **dissipation** (THOMSON [38]). It is described by the **second law of thermodynamics**, which was discovered by CLAUSIUS [15]. In our context, we derive the second law as follows.

When viewing the Euler inequality (2) together with the Euler equation (4), parts (iii)-(iv) of Definition 1.1 say that if S, V, n are conserved (thermal, mechanical and chemical isolation) then the **internal energy**,

$$U := TS - PV + \mu \cdot n \tag{17}$$

is minimal in equilibrium. If T, V, n are conserved (mechanical and chemical isolation of a system at constant temperature T) then the **Helmholtz (free) energy**,

$$F := U - TS = -PV + \mu \cdot n$$

is minimal in equilibrium. If T, P, n are conserved (chemical isolation of a system at constant temperature T and pressure P) then the **Gibbs (free) energy**,

$$G := F + PV = \mu \cdot n$$

is minimal in equilibrium. If S, P, n are conserved (thermal and chemical isolation of a system at constant pressure P) then the **enthalpy**

$$H := U + PV = TS + \mu \cdot n$$

is minimal in equilibrium. These rules just express the nondynamical part of the content of the second law since, in equilibrium thermodynamics, dynamical questions are ignored.

Finally, the **third law of thermodynamics**, due to NERNST [29], says that the entropy is nonnegative. In view of (3), this is equivalent to the monotonicity of $\Delta(T, P, \mu)$ with respect to T.

3   Consequences of the first law

The first law of thermodynamics describes the observable energy balance in a reversible process. The total energy flux dU into the system is composed of the **thermal energy flux** or **heat flux** TdS, the **mechanical energy flux** $-PdV$, and the **chemical energy flux** $\mu \cdot dn$.

The Gibbs-Duhem equation (15) describes the energy balance necessary to compensate the changes $d(TS) = TdS + SdT$ of thermal energy, $d(PV) = PdV + VdP$ of mechanical energy, and $d(\mu \cdot n) = \mu \cdot dn + n \cdot d\mu$ of chemical energy in the energy contributions to the Euler equation to ensure that the Euler equation remains valid during a reversible transformation. Indeed, the Gibbs-Duhem equation and the first law (16) together imply that $d(TS - PV + \mu \cdot n - U)$ vanishes, which expresses the invariance of the Euler equation (i.e., the equilibrium condition) under arbitrary reversible transformations.

Related to the various energy fluxes are the **thermal work**

$$Q = \int T(\lambda) dS(\lambda),$$

the **mechanical work**

$$W_{\mathrm{mech}} = -\int P(\lambda) dV(\lambda),$$

and the **chemical work**

$$W_{\mathrm{chem}} = \int \mu(\lambda) \cdot dn(\lambda)$$

performed in a reversible transformation. The various kinds of work generally depend on the path through the state space; however, the mechanical work depends only on the end points if the associated process is conservative.

As is apparent from the formulas given, thermal work is done by changing the entropy of the system, mechanical work by changing the volume, and chemical work by changing the mole numbers. In particular, in case of thermal, mechanical, or chemical **isolation**, the corresponding fluxes vanish identically. Thus, constant S characterizes **adiabatic**, i.e., thermally isolated systems, constant V characterizes mechanically isolated systems, and constant n characterizes **closed**[7] (or **impermeable**) i.e., chemically isolated systems. Note that this constancy only holds when all assumptions for a standard system are valid: global equilibrium, a single phase, and the absence of chemical reactions. Of course, these **boundary conditions** are somewhat idealized situations. But they can be approximately realized in practice and are of immense scientific and technological importance.

The first law shows that, in appropriate units, the temperature T is the amount of internal energy needed to increase the entropy S in a mechanically and chemically isolated system by one unit. The pressure P is, in appropriate units, the amount of internal energy needed to decrease the volume V in a thermally and chemically isolated system by one unit. In particular, increasing pressure decreases the volume; this explains the minus sign in the definition of P. The chemical potential μ_j is, in appropriate units, the amount of internal energy needed to increase the mole number n_j in a thermally and mechanically isolated system by one unit. With the traditional units, temperature, pressure, and chemical potentials are no longer energies.

We see that the entropy and the volume behave just like the mole number. This analogy can be deepened by observing that mole numbers are the natural measure of the amounts of "matter" of each kind in a system, and chemical energy flux is accompanied by adding or removing matter. Similarly, volume is the natural measure of the amount of "space" a system occupies, and mechanical energy flux in a standard system is accompanied by adding or removing space. Thus we may regard entropy as the natural measure of the amount of "heat" (colloquial) contained in a system[8], since thermal energy flux is accompanied by adding or removing heat. Looking at other extensive quantities, we also recognize energy as the natural measure of the amount of "power" (colloquial), momentum as the natural measure of the amount of "force" (colloquial), and mass as the natural measure of the amount of "inertia" (colloquial) of a system. In each case, the notions in quotation marks are the colloquial terms which are associated in ordinary life with the more precise, formally defined physical quantities. For historical reasons, the words heat, power, and force are used in physics with a meaning different from the colloquial terms "heat", "power", and "force".

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[7]Note that the terms 'closed system' has also a much more general interpretation – which we do *not* use in this chapter –, namely as a conservative dynamical system.

[8]Thus, entropy is the modern replacement for the historical concepts of **phlogiston** and **caloric**, which explained some heat phenomena but failed to give a fully correct account of them. Phlogiston turned out to be "missing oxygen", an early analogue of the picture of positrons as "missing electrons", holes in the Dirac sea. Caloric was a massless substance of heat which had almost the right properties, explained many effects correctly, and fell out of favor only after it became known that caloric could be generated in arbitrarily large amounts from mechanical energy, thus discrediting the idea of heat being a substance. (For the precise relation of entropy and caloric, see KUHN [24, 25], WALTER [40], and the references quoted there.) In the modern picture, the extensivity of entropy models the substance-like properties of the colloquial term "heat". But as there are no particles of space whose mole number is proportional to the volume, so there are no particles of heat whose mole number is proportional to the entropy. Nevertheless, the introduction of heat particles on a formal level has some uses; see, e.g., STREATER [37].

4 Consequences of the second law

The second law is centered around the impossibility of perpetual motion machines due to the inevitable loss of energy by dissipation such as friction (see, e.g., BOWDEN & LEBEN [8]) or uncontrolled radiation. This means that – unless continually provided from the outside – energy is lost with time until a metastable state is attained, which usually is an equilibrium state. Therefore, the energy at equilibrium is minimal under the circumstances dictated by the boundary conditions discussed before, which define the quantities held constant. In a purely kinematic setting as in our treatment, the approach to equilibrium cannot be studied, and only the minimal energy principles – one for each set of boundary conditions – remain.

Traditionally, the second law is often expressed in the form of an extremal principle for some thermodynamic potential. For a complete list of thermodynamic potentials used in practice, see ALBERTY [2]. We derive here only the extremal principles for the internal energy, the Helmholtz energy, and the Gibbs energy,[9] which give rise to the **internal energy potential**

$$U(S, V, n) := \max_{T, P, \mu} \{ TS - PV + \mu \cdot n \mid \Delta(T, P, \mu) = 0; T > 0 \}, \tag{18}$$

the **Helmholtz potential**

$$F(T, V, n) := \max_{P, \mu} \{ -PV + \mu \cdot n \mid \Delta(T, P, \mu) = 0 \}, \tag{19}$$

and the **Gibbs potential**

$$G(T, P, n) := \max_{\mu} \{ \mu \cdot n \mid \Delta(T, P, \mu) = 0 \}. \tag{20}$$

The arguments on the left hand side define the variables kept constant.

The Gibbs potential is of particular importance since everyday processes frequently happen at approximately constant temperature, pressure, and mole number.

4.1 Theorem. (*Extremal principles*)
(i) In an arbitrary state,
$$U \geq U(S, V, n), \tag{21}$$

with equality iff the state is an equilibrium state. The remaining thermodynamic variables are then given by

$$T = \frac{\partial}{\partial S} U(S, V, n), \quad P = -\frac{\partial}{\partial V} U(S, V, n), \quad \mu = \frac{\partial}{\partial n} U(S, V, n), \quad U = U(S, V, n).$$

In particular, an equilibrium state is uniquely determined by the values of S, V, and n.

(ii) In an arbitrary state,
$$U - TS \geq F(T, V, n), \tag{22}$$

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[9]The different potentials are related by so-called **Legendre transforms**; cf. ROCKAFELLAR [35] for the mathematical properties of Legendre transforms, ARNOL'D [5] for their application in mechanics, and ALBERTY [2] for their application in chemistry.

with equality iff the state is an equilibrium state. The remaining thermodynamic variables are then given by

$$S = -\frac{\partial F}{\partial T}(T, V, n), \quad P = -\frac{\partial F}{\partial V}(T, V, n), \quad \mu = \frac{\partial F}{\partial n}(T, V, n),$$

$$U = F(T, V, n) + TS.$$

In particular, an equilibrium state is uniquely determined by the values of T, V, and n.

(iii) In an arbitrary state,

$$U - TS + PV \geq G(T, P, n), \tag{23}$$

with equality iff the state is an equilibrium state. The remaining thermodynamic variables are then given by

$$S = -\frac{\partial G}{\partial T}(T, P, n), \quad V = \frac{\partial G}{\partial P}(T, P, n), \quad \mu = \frac{\partial G}{\partial n}(T, P, n),$$

$$U = G(T, P, n) + TS - PV.$$

In particular, an equilibrium state is uniquely determined by the values of T, P, and n.

Proof. We prove (ii); the other two cases are entirely similar. (22) and the statement about equality are a direct consequence of Definition 1.1(iii)–(iv). Thus, the difference $U - TS - F(T, V, n)$ takes its minimum value zero at the equilibrium value of T. Therefore, the derivative with respect to T vanishes, which gives the formula for S. To get the formulas for P and μ, we note that for constant T, the first law (16) implies

$$dF = d(U - TS) = dU - TdS = -PdV + \mu \cdot dn.$$

For a reversible transformation which only changes P or μ_j, we conclude that $dF = -PdV$ and $dF = \mu_j dn_j$, respectively. Solving for P and μ_j, respectively, implies the formulas for P and μ_j. $\qquad\square$

The above results imply that one can regard each thermodynamic potential as a complete alternative way to describe the manifold of thermal states and hence all equilibrium properties. This is very important in practice, where one usually describes thermodynamic material properties in terms of the Helmholtz or Gibbs potential, using models like NRTL (RENON & PRAUSNITZ [33], PRAUSNITZ et al. [30]) or SAFT (CHAPMAN et al. [11, 12]). The description in terms of the system function Δ, although more fundamental from a theoretical perspective, is less useful since it expresses all quantities in terms of (temperature, pressure, and) chemical potentials, and the latter are usually not directly accessible.

The additivity of extensive quantities is reflected in the corresponding properties of the thermodynamic potentials:

4.2 Theorem. *The potentials $U(S, V, n)$, $F(T, V, n)$, and $G(T, P, n)$ satisfy, for real $\lambda, \lambda^1, \lambda^2 \geq 0$,*

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n), \tag{24}$$

$$F(T, \lambda V, \lambda n) = \lambda F(T, V, n), \qquad (25)$$

$$G(T, P, \lambda n) = \lambda G(T, P, n), \qquad (26)$$

$$U(\lambda^1 S^1 + \lambda^2 S^2, \lambda^1 V^1 + \lambda^2 V^2, \lambda^1 n^1 + \lambda^2 n^2) \le \lambda^1 U(S^1, V^1, n^1) + \lambda^2 U(S^2, V^2, n^2), \qquad (27)$$

$$F(T, \lambda^1 V^1 + \lambda^2 V^2, \lambda^1 n^1 + \lambda^2 n^2) \le \lambda^1 F(T, V^1, n^1) + \lambda^2 F(T, V^2, n^2), \qquad (28)$$

$$G(T, P, \lambda^1 n^1 + \lambda^2 n^2) \le \lambda^1 G(T, P, n^1) + \lambda^2 G(T, P, n^2). \qquad (29)$$

In particular, U convex in S, V, and n, F is convex in V, and n, and G is convex in n.

Proof. The first three equations express homogeneity and are a direct consequence of the definitions. Inequality (28) holds since, for suitable P and μ,

$$\begin{aligned}
F(T, \lambda^1 V^1 + \lambda^2 V^2, \lambda^1 n^1 + \lambda^2 n^2) &= -P(\lambda^1 V^1 + \lambda^2 V^2) + \mu \cdot (\lambda^1 n^1 + \lambda^2 n^2) \\
&= \lambda^1(-PV^1 + \mu \cdot n^1) + \lambda^2(-PV^2 + \mu \cdot n^2) \\
&\le \lambda^1 F(T, V^1, n^1) + \lambda^2 F(T, V^2, n^2);
\end{aligned}$$

and the others follow in the same way. Specialized to $\lambda^1 + \lambda^2 = 1$, the inequalities express the claimed convexity. $\qquad\square$

For a system at constant temperature T, pressure P, and mole number n, consisting of a number of parts labeled by a superscript k which are separately in equilibrium, the Gibbs energy is extensive (i.e., additive under composition of disjoint subsystems), since

$$\begin{aligned}
G &= U - TS + PV = \sum U^k - T \sum S^k + P \sum V^k \\
&= \sum (U^k - TS^k + PV^k) = \sum G^k.
\end{aligned}$$

Equilibrium requires that $\sum G^k$ is minimal among all choices with $\sum n^k = n$, and by introducing a Lagrange multiplier vector μ^* for the constraints, we see that in equilibrium, the derivative of $\sum(G(T, P, n^k) - \mu^* \cdot n^k)$ with respect to each n^k must vanish. This implies that

$$\mu^k = \frac{\partial G}{\partial n^k}(T, P, n^k) = \mu^*.$$

Thus, in equilibrium, all μ^k must be the same. At constant T, V, and n, one can apply the same argument to the Helmholtz potential, at constant S, V, and n to the internal energy potential, and at constant S, P, and n to the enthalpy. In each case, the equilibrium is characterized by the constancy of the intensive parameters.

The second law may also be expressed in terms of entropy.

4.3 Theorem. *(Entropy form of the second law)*
In an arbitrary state of a standard thermodynamic system

$$S \le S(U, V, n) := \min \{T^{-1}(U + PV - \mu \cdot n) \mid \Delta(T, P, \mu) = 0\},$$

with equality iff the state is an equilibrium state. The remaining thermal variables are then given by

$$T^{-1} = \frac{\partial S}{\partial U}(U, V, n), \quad T^{-1}P = \frac{\partial S}{\partial V}(U, V, n), \quad T^{-1}\mu = -\frac{\partial S}{\partial n}(U, V, n), \tag{30}$$

$$U = TS(T, V, n) - PV + \mu \cdot n. \tag{31}$$

Proof. This is proved in the same way as Theorem 4.1. □

This result – perhaps the most famous but also most misunderstood version of the second law – implies that when a system in which U, V and n are kept constant reaches equilibrium, the entropy must have increased. Unfortunately, the assumption of constant U, V and n is unrealistic; such constraints are not easily realized in nature. Under different constraints[10], the entropy is no longer maximal.

The degree to which macroscopic space and time correlations are absent characterizes the amount of **macroscopic disorder** of a system. Global equilibrium states are therefore macroscopically highly uniform; they are the most ordered macroscopic states in the universe rather than the most disordered ones. A system not in global equilibrium is characterized by macroscopic local inhomogeneities, indicating that the space-independent global equilibrium variables alone are not sufficient to describe the system. Its intrinsic complexity is apparent only in a microscopic treatment. The only macroscopic shadow of this complexity is the critical opalescence of fluids near a critical point (ANDREWS [4], FORSTER [16]). The contents of the second law of thermodynamics for global equilibrium states may therefore be phrased informally as follows: *In global equilibrium, macroscopic order (homogeneity) is perfect and microscopic complexity is maximal.*

In particular, the traditional interpretation of entropy as a measure of disorder is often misleading. Much more carefully argued support for this statement, with numerous examples from teaching practice, is in LAMBERT [26]. In systems with several phases, a naive interpretation of the second law as tendency moving systems towards increasing disorder is even more inappropriate: A mixture of water and oil spontaneously separates, thus "ordering" the water molecules and the oil molecules into separate phases!

Thus, while the second law in the form of a maximum principle for the entropy has some theoretical and historical relevance, it is not the extremal principle ruling nature. The irreversible nature of physical processes is instead manifest as **energy dissipation** which, in a microscopic interpretation, indicates the loss of energy to the unmodelled microscopic

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[10]For example, if one pours milk into a cup of coffee, stirring mixes coffee and milk, thus increasing complexity. Macroscopic order is restored after some time when this increased complexity has become macroscopically inaccessible. Since T, P and n are constant, the cup of coffee ends up in a state of minimal Gibbs energy, and not in a state of maximal entropy! More formally, the first law shows that, for standard systems at fixed value of the mole number, the value of the entropy decreases when U or V (or both) decrease reversibly; this shows that the value of the entropy may well decrease if accompanied by a corresponding decrease of U or V. The same holds out of equilibrium (though our equilibrium argument no longer applies). For example, though it decreases the entropy, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ may happen spontaneously at constant $T = 25°C$ and $P = 1$ atm if appropriately catalyzed.

degrees of freedom.[11] Macroscopically, the global equilibrium states are therefore states of least free energy, the correct choice of which depends on the boundary condition, with the least possible freedom for change. This macroscopic immutability is another intuitive explanation for the maximal macroscopic order in global equilibrium states.

5 The approach to equilibrium

Using only the present axioms, one can say a little bit about the behavior of a system close to equilibrium in the following, idealized situation. Suppose that a system at constant S, V, and n which is close to equilibrium at some time t reaches equilibrium at some later time t^*. Then the second law implies

$$0 \leq U(t) - U(t^*) \approx (t - t^*)\frac{dU}{dt},$$

so that $dU/dt \leq 0$. We assume that the system is composed of two parts, which are both in equilibrium at times t and t^*. Then the time shift induces on both parts a reversible transformation, and the first law can be applied to them. Thus

$$dU = \sum_{k=1,2} dU^k = \sum_{k=1,2}(T^k dS^k - P^k dV^k + \mu^k \cdot dn^k).$$

Since S, V, and n remain constant, we have $dS^1 + dS^2 = 0$, $dV^1 + dV^2 = 0$, $dn^1 + dn^2 = 0$, and since for the time shift $dU \leq 0$, we find the inequality

$$0 \geq (T^1 - T^2)dS^1 - (P^1 - P^2)dV^1 + (\mu^1 - \mu^2) \cdot dn^1.$$

This inequality gives information about the direction of the flow in case that all but one of the extensive variables are known to be fixed.

In particular, at constant V^1 and n^1, we have $dS^1 \leq 0$ if $T^1 > T^2$; i.e., "heat" (entropy) flows from the hotter part towards the colder part. At constant S^1 and n^1, we have $dV^1 \leq 0$ if $P^1 < P^2$; i.e., "space" (volume) flows from lower pressure to higher pressure: the volume of the lower pressure part decreases and is compensated by a corresponding increase of the volume in the higher pressure part. And for a pure substance at constant S^1 and V^1, we have $dn^1 \leq 0$ if $\mu^1 > \mu^2$; i.e., "matter" (mole number) flows from higher chemical potential towards lower chemical potential. These qualitative results give temperature, pressure, and chemical potential the familiar intuitive interpretation.

This glimpse on nonequilibrium properties is a shadow of the far reaching fact that, in nonequilibrium thermodynamics, the intensive variables behave like potentials whose gradients induce forces that tend to diminish these gradients, thus enforcing (after the time needed to reach equilibrium) agreement of the intensive variables of different parts of a

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[11]An example is friction, where macroscopic kinetic energy is translated into random motion of the molecules. Their details are not modelled in a thermal description, and only their mean properties are reflected – via the so-called equipartition theorem – in the temperature.

system. In particular, temperature acts as a thermal potential, whose differences create thermal forces which induce thermal currents, a flow of "heat" (entropy), in a similar way as differences in electrical potentials create electrical currents, a flow of "electricity" (electrons)[12]. While these dynamical issues are outside the scope of the present work, they motivate the fact that one can control some intensive parameters of the system by controlling the corresponding intensive parameters of the environment and making the walls permeable to the corresponding extensive quantities. This corresponds to standard procedures familiar to everyone from ordinary life, such as heating to change the temperature, applying pressure to change the volume, or immersion into a substance to change the chemical composition.

The stronger nonequilibrium version of the second law says that (for suitable boundary conditions) equilibrium is actually attained after some time (strictly speaking, only in the limit of infinite time). This implies that the energy difference

$$\delta E := U - U(S, V, n) = U - TS - F(T, V, n) = U - TS + PV - G(T, P, n)$$

is the amount of energy that is dissipated in order to reach equilibrium. In an equilibrium setting, we can only compare what happens to a system prepared in a nonequilibrium state assuming that, subsequently, the full energy difference δE is dissipated so that the system ends up in an equilibrium state. Since few variables describe everything of interest, this constitutes the power of equilibrium thermodynamics. But this power is limited, since equilibrium thermodynamics is silent about when – or whether at all – equilibrium is reached. Indeed, in many cases, only metastable states are reached, which change too slowly to ever reach equilibrium on a human time scale. Typical examples of this are crystal defects, which constitute nonglobal minima of the free energy – the global minimum would be a perfect crystal.

A   Convexity

The mathematics of thermodynamics makes essential use of the concept of convexity. A set $X \subseteq \mathbb{R}^n$ is called **convex** if $tx + (1 - t)y \in X$ for all $x, y \in X$ and all $t \in [0, 1]$. A real-valued function ϕ is called **convex** on the convex set $X \subseteq \mathbb{R}^n$ if ϕ is defined on X and, for all $x, y \in X$,

$$\phi(tx + (1 - t)y) \leq t\phi(x) + (1 - t)\phi(y) \quad \text{for } 0 \leq t \leq 1.$$

If x is written explicitly as several arguments (such as T, P, μ in the main text), one says that ϕ is **jointly convex** in these arguments. Clearly, ϕ is convex iff for all $x, y \in X$, the function $\mu : [0, 1] \to \mathbb{R}$ defined by

$$\mu(t) := \phi(x + t(y - x))$$

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[12]See FUCHS [18] for a thermodynamics course (and for a German course JOB [22]) thoroughly exploiting these parallels.

is convex. It is well-known that, for twice continuously differentiable ϕ, this is the case iff the second derivative $\mu''(t)$ is nonnegative for $0 \leq t \leq 1$. Note that by a theorem of Aleksandrov (see ALEKSANDROV [3], ALBERTI & AMBROSIO [1], ROCKAFELLAR [34]), convex functions are almost everywhere twice continuously differentiable: For almost every $x \in X$, there exist a unique vector $\partial\phi(x) \in \mathbb{R}^n$, the **gradient** of ϕ at x, and a unique symmetric, positive semidefinite matrix $\partial^2\phi(x) \in \mathbb{R}^{n \times n}$, the **Hessian** of ϕ at x, such that

$$\phi(x + h) = \phi(x) + h^T\partial\phi(x) + \frac{1}{2}h^T\partial^2\phi(x)h + o(\|h\|^2)$$

for sufficiently small $h \in \mathbb{R}^n$. A function ϕ is called **concave** if $-\phi$ is convex. Thus, for a twice continuously differentiable function ϕ of a single variable τ, ϕ is concave iff $\mu''(\tau) \leq 0$ for $0 \leq \tau \leq 1$.

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