

# On the foundations of thermodynamics

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**Abstract.** On the basis of new, concise foundations, this paper establishes the four laws of thermodynamics, the Maxwell relations, and the stability requirements for response functions, in a form applicable to global (homogeneous), local (hydrodynamic) and microlocal (kinetic) equilibrium.

The present, self-contained treatment needs very little formal machinery and stays very close to the formulas as they are applied by the practicing physicist, chemist, or engineer. From a few basic assumptions, the full structure of phenomenological thermodynamics and of classical and quantum statistical mechanics is recovered.

Care has been taken to keep the foundations free of subjective aspects (which traditionally creep in through information or probability). One might describe the paper as a uniform treatment of the nondynamical part of classical and quantum statistical mechanics “without statistics” (i.e., suitable for the definite descriptions of single objects) and “without mechanics” (i.e., independent of microscopic assumptions). When enriched by the traditional examples and applications, this paper may serve as the basis for a course on thermal physics.

**Keywords:** density, energy balance, energy dissipation, entropy, equation of state, equilibrium state, equilibrium thermodynamics, Euclidean \*-algebra, Euler equation, exponential family, extremal principles, foundations of thermodynamics, free energy, Gibbs paradox, Gibbs state, Gibbs-Bogoliubov inequality, information deficit, Kubo inner product, Legendre transform, limit resolution, partition function, quantization, response functions, Schrödinger equation, second law of thermodynamics, thermal interpretation of quantum mechanics, thermal state, thermodynamic stability, unobservable complexity

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# 1 Introduction

It is worthwhile to have the structural properties of physical theories spelled out independent of computational techniques for obtaining quantitatively correct numbers from the assumptions made. This allows one to focus attention on the simplicity and beauty of theoretical physics, which is often hidden in a jungle of techniques for estimating or calculating approximations for quantities of interests. The standard approximation machinery for calculating explicit thermodynamic properties of materials from first principles can be postponed to a later stage where one actually wants to do quantitative predictions of macroscopic properties from microscopic assumptions.

In the present paper, a treatment of equilibrium statistical mechanics and the kinematic part of nonequilibrium statistical mechanics is given which shows that such a structural point of view leads to great conceptual simplifications: From a single basic assumption (Definition 7.1), the full structure of phenomenological thermodynamics and of statistical mechanics is recovered (except for the third law which requires an additional quantization assumption), compatible with both a classical or a quantum microscopic view, but without the elaborate formalism needed to do actual statistical mechanics calculations. (In this paper, these are only hinted at, as a comment on the cumulant expansion.)

Our treatment is self-contained and stays very close to the formulas as they are applied by the practicing physicist, chemist, or engineer. It needs very little formal machinery, in contrast to other axiomatic settings for thermodynamics (e.g., LIEB & YNGVASON [80]). A different, well-known axiomatic foundation of (classical) thermodynamics was given by CARATHÉODORY [28]. See also EMCH & LIU [41].

In contrast to traditional treatments of thermodynamics (e.g., HAKEN [57], JAYNES [64], KATZ [70]), we do not *assume* the basic thermodynamical laws and relations but *derive* them from simple definitions. In our treatment, the zeroth law is made precise as a definition, and each of the other three laws becomes a theorem. All formulas are valid rigorously without approximation, assuming only that the states in question are thermal states.

Since thermodynamics is completely observer independent, its foundations should have this feature, too. Therefore, care has been taken to keep the foundations free of subjective aspects, traditionally introduced by an information theoretic approach (see BALIAN [9] for a recent exposition) to statistical mechanics in terms of the knowledge of an observer. The present approach shows that (and in which sense) a fully objective, observer-independent foundation is possible.

One might describe the paper as a uniform treatment of the nondynamical part of classical and quantum statistical mechanics “without statistics and probability” (i.e., suitable for the definite descriptions of single objects) and “without mechanics” (i.e., independent of microscopic assumptions). Essentially, the paper develops all relevant results without assuming or claiming anything definite about the meaning of the quantities assumed to exist

on the fundamental description level. Thus the interpretation of an underlying microscopic structure is left completely open; even the 'number of particles' can be taken figuratively!

Avoiding a definite mechanical picture frees the foundations from the unresolved (and in principle unresolvable) issues regarding the truly fundamental constituents of nature and possibly needed modifications of quantum field theory at the Planck scale where gravitational effects must be taken into account. Avoiding probability implies that the traditional foundational problems of quantum mechanics – the most informative sources include STAPP [118], BALLENTINE [10], HOME & WHITAKER [60], PERES & TERNO [101] and the reprint collection by WHEELER & ZUREK [129] – and of equilibrium statistical mechanics, carefully analyzed by SKLAR [115] for classical mechanics, (see also GRANDY [52] and the older surveys by EHRENFEST [39], TER HAAR [121], PENROSE [99]), and by WALLACE [127] for quantum mechanics, do not affect the foundations of thermodynamics.

This is one of a sequence of papers designed to give a mathematically precise and philosophically consistent foundation of modern theoretical physics. The ultimate goal are foundations of physics which are fully objective, mathematically concise, and describe the universe as a whole, including at times when human observers could not exist. The first paper in the series (NEUMAIER [93]) defines and discusses the concepts of quantities, ensembles, and experiments in classical and quantum physics.

On this basis (but formally independent), the present paper derives the standard formalism of equilibrium thermodynamics and statistical mechanics, formulated in a way that includes global equilibrium (homogeneous materials), local equilibrium (hydrodynamics and continuum mechanics), microlocal equilibrium (kinetic descriptions), and quantum equilibrium (microscopic descriptions). In this paper, only the kinematical level is discussed; another paper (NEUMAIER [94]) on the dynamics of thermal states is in preparation. The formalism developed is closely related to the theory of exponential families (cf. BARNDORFF-NIELSEN [11, 12], BERNARDO & SMITH [17]), although the language used there is completely different.

The physics of our results is, of course, well-known since GIBBS [48]; see UFFINK [126] for a history. However, the treatment of the material is new, as is the careful set-up used to arrive at the standard results. In particular: We make precise (in Section 2) to which extent thermodynamical variables have a meaning outside equilibrium, thus ensure a formally well-defined second law. We give (in Section 6) a new interpretation of the notion of an ensemble, valid for single macroscopic systems, whose properties are well-defined without reference to multiple realizations, and clarify the role of statistics in the foundations. We give (in Sections 7, 10, 11, and 12) concise formal statements of the fundamental laws of thermodynamics. Finally, we demonstrate (in Section 12) that the conventional wave function form of quantum mechanics can be simply understood as the low temperature limit of thermodynamics.

The paper is organized as follows: To set the physical background needed to appreciate the remainder of the paper, Section 2 and Section 3 give a description of standard phenomenological equilibrium thermodynamics for single-phase systems in the absence of chemical reactions and electromagnetic fields. The present, unconventional approach summarizes the assumptions needed in a way that allows an easy comparison with statistical mechanics. Section 4 introduces Gibbs states, in a generality covering both the classical and the quantum case; their abstract properties are studied in Section 5. Section 6 discusses the role of statistics in our approach. Section 7 defines thermal states and discusses their relevance for global, local, and microlocal equilibrium. Section 8 deduces the existence of an equation of state and connects the results to the phenomenological exposition in Section 2. Section 9 discusses questions relating to different thermal description levels. Section 10 proves the first law of thermodynamics. In Sections 11, we compare thermal states with arbitrary Gibbs states and deduce the extremal principles of the second law. Section 12 shows that the third law is related to a simple quantization condition for the entropy and relates it to the time-independent Schrödinger equation. Section 13 discusses the hierarchy of equilibrium descriptions and how they relate to each other.

Appendix A exhibits the relations to information theory, by putting a simple decision problem into our framework. In this example, we recover the usual interpretation of the value of the entropy as a measure of unobservable internal complexity (lack of information). Appendix B discusses the maximum entropy principle and its limitations. Appendix C contains the proofs of a few auxiliary results needed in the main text.

In this paper, we shall denote quantities with a specific meaning by capital letters, conforming to the tradition in thermodynamics.

The level of formal precision is somewhere between that of mathematical physics and that of most treatments of theoretical physics. I made my best efforts to carefully argue all relevant issues and to make explicit all assumptions used in these arguments. Definitions, theorems, and proofs are stated precisely. However, to avoid an excessive mathematical apparatus we do not specify the domains of definition of functions, and we state but do not use axioms relating to continuity properties and similar things, though these would be necessary for a completely rigorous treatment. If one assumes that the algebra of quantities is finite-dimensional, all proofs are valid rigorously as stated. For the infinite dimensional case, these arguments need further justification. However, assuming the results in Appendix C, all other results still follow rigorously. (In fact, it can be shown that everything would hold rigorously when this algebra is embeddable into a  $C^*$ -algebra. But the applications require certain unbounded operators to occur. Moreover, unlike our nearly trivial axioms, the  $C^*$ -algebra axioms have no intuitive physical basis, but are abstracted from mathematical properties of algebras of bounded operators on Hilbert spaces. Thus, we do not use the  $C^*$ -algebra framework.)

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## 2 Phenomenological thermodynamics

To introduce the physical background for our developments, we discuss thermodynamic systems which describe the single-phase global equilibrium of matter in the absence of chemical reactions and electromagnetic fields. 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. (Multiple phases would be only piecewise homogeneous; each phase separately is described as indicated, but discussing the equilibrium at interfaces needs some additional effort, described in all textbooks on thermodynamics.)

Our phenomenological approach is similar to that of CALLEN [26], a widely accepted authority on equilibrium thermodynamics, who introduces the basic concepts by means of a few postulates from which everything else follows. The present setting has the advantage that it easily matches the more fundamental approach based on statistical mechanics. Our axioms are also slightly more precise than Callen's in that they specify the kinematical properties of states outside equilibrium. This enables us to replace his informal thermodynamic stability arguments (which depends on dynamical assumption close to equilibrium) by rigorous mathematical arguments.

The species of molecules of fixed chemical composition are labeled by an index  $j \in J$ ; we speak of **particles of species  $j$** . A standard thermodynamic system is characterized by the **number  $N_j$  of particles** of each species  $j$ , the corresponding **chemical potential  $\mu_j$**  of species  $j$ , the **volume  $V$** , the **pressure  $P$** , the **temperature  $T$** , the **entropy  $S$** , and the **Hamilton energy  $H$** . These variables, the **extensive** variables  $N_j, V, S, H$  and the **intensive** variables  $\mu_j, P, T$ , are jointly called the **basic thermodynamic variables**. In the terminology, we mainly follow the IUPAC convention (ALBERTY [1, Section 7]), except that we use the letter  $H$  to denote the Hamilton energy, as customary in quantum mechanics. In equilibrium,  $H$  equals the internal energy. The Hamilton energy should not be confused with the enthalpy which (is usually denoted by  $H$  but here) is given in equilibrium by  $H + PV$ . (For a history of thermodynamics notation, see BATTINO et al. [13].)

As customary in thermodynamics, we allow the  $N_j$  to have arbitrary nonnegative real values, not only integers. (Chemists use instead of particle numbers the corresponding mole numbers, which differ by a fixed numerical factor, the Avogadro constant; cf. Example 2.3.) We group the  $N_j$  and the  $\mu_j$  into vectors  $N$  and  $\mu$  indexed by  $J$  and write  $\mu \cdot N = \sum_{j \in J} \mu_j N_j$ . If there is just a single species, we drop the indices and have  $\mu \cdot n = \mu N$ . In this section, all numbers are real.

Equilibrium thermodynamics is about characterizing so-called equilibrium states and comparing them with similar nonequilibrium states. Everything of relevance in equilibrium thermodynamics can be deduced from the following

**2.1 Definition. (Axioms for phenomenological thermodynamics)**

(i) Temperature  $T$ , pressure  $P$ , volume  $V$  are positive, particle numbers  $N_j$  are nonnegative. There is a convex<sup>1</sup> **system function**  $\Delta$  of the intensive variables  $(T, P, \mu)$  which is monotone increasing in  $T$  and monotone decreasing in  $P$ , such that the intensive variables are related by the **equation of state**

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

The set of  $(T, P, \mu)$  satisfying  $T > 0$ ,  $P > 0$  and the equation of state is called the **state space**.

(ii) Outside equilibrium, only the extensive variables are well-defined; they are additive under the composition of disjoint subsystems. The Hamilton energy  $H$  satisfies the **Euler inequality**

$$H \geq TS - PV + \mu \cdot N \tag{2}$$

for all  $(T, P, \mu)$  in the state space. **Equilibrium states** have well-defined intensive and extensive variables, and are defined by equality in (2).

This is the complete list of assumptions which define phenomenological equilibrium thermodynamics; the system function  $\Delta$  can be determined either by fitting to experimental data, or by calculation from more fundamental descriptions, cf. Theorem 8.1. All other properties follow from the system function. Thus, the equilibrium properties of a material (e.g., "salty water",  $J = \{\text{salt, water}\}$ ) are characterized by the system function  $\Delta$ ; each equilibrium instance of the material ("this glass of salty water") is characterized by a particular state  $(T, P, N)$ , from which all equilibrium properties can be computed:

**2.2 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**

$$H = TS - PV + \mu \cdot N, \tag{4}$$

where  $\Omega$  is a positive number called the **system size**.

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<sup>1</sup>See Appendix C for convexity and the associated differentiability almost everywhere. Surfaces of nondifferentiability correspond to so-called **phase transitions**. Although practically important and hence discussed in every textbook of thermodynamics, phase transitions do not raise foundational problems. Therefore, we look in this paper only at regions of state space where  $\Delta$  is twice continuously differentiable.

(ii) In equilibrium, we have the **Maxwell reciprocity relations**

$$-\frac{\partial V}{\partial T} = \frac{\partial S}{\partial P}, \quad \frac{\partial N_j}{\partial T} = \frac{\partial S}{\partial \mu_j}, \quad \frac{\partial N_j}{\partial P} = -\frac{\partial V}{\partial \mu_j}, \quad \frac{\partial N_j}{\partial \mu_k} = \frac{\partial N_k}{\partial \mu_j} \quad (5)$$

and the **stability conditions**

$$\frac{\partial S}{\partial T} \geq 0, \quad \frac{\partial V}{\partial P} \leq 0, \quad \frac{\partial N_j}{\partial \mu_j} \geq 0. \quad (6)$$

*Proof.* In equilibrium, at fixed  $S, V, N$ , the triple  $(T, P, \mu)$  is a maximizer of  $TS - PV + \mu \cdot N$  under the constraints  $\Delta(T, P, \mu) = 0, T > 0, P > 0$ . 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  $\Omega$ . Setting the partial derivatives to zero gives (3), and since the maximum is attained in equilibrium, the Euler equation (4) follows. The system size  $\Omega$  is positive since  $V > 0$  and  $\Delta$  is decreasing in  $P$ . Since the Hessian matrix of  $\Delta$ ,

$$\Sigma = \begin{pmatrix} \frac{\partial^2 \Delta}{\partial T^2} & \frac{\partial^2 \Delta}{\partial P \partial T} & \frac{\partial^2 \Delta}{\partial \mu \partial T} \\ \frac{\partial^2 \Delta}{\partial T \partial P} & \frac{\partial^2 \Delta}{\partial P^2} & \frac{\partial^2 \Delta}{\partial \mu \partial P} \\ \frac{\partial^2 \Delta}{\partial T \partial \mu} & \frac{\partial^2 \Delta}{\partial P \partial \mu} & \frac{\partial^2 \Delta}{\partial \mu^2} \end{pmatrix} = \Omega^{-1} \begin{pmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial P} & \frac{\partial S}{\partial \mu} \\ -\frac{\partial V}{\partial T} & -\frac{\partial V}{\partial P} & -\frac{\partial V}{\partial \mu} \\ \frac{\partial N}{\partial T} & \frac{\partial N}{\partial P} & \frac{\partial N}{\partial \mu} \end{pmatrix},$$

is symmetric, the Maxwell reciprocity relations follow, and since  $\Delta$  is convex,  $\Sigma$  is positive semidefinite; hence the diagonal elements of  $\Sigma$  are nonnegative, giving the stability conditions.  $\square$

Note that there are further stability conditions since the determinants of all principal submatrices of  $\Sigma$  must be nonnegative. Also,  $N_j \geq 0$  implies that  $\Delta$  is monotone increasing in each  $\mu_j$ .

**2.3 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

$$\Delta(T, P, \mu) = \sum_{j \in J} \pi_j(T) e^{\mu_j / kT} - P, \quad (7)$$

where the  $\pi_j(T)$  are positive functions of the temperature,  $k$  is the **Boltzmann constant** and we use the bracketing convention  $\mu_j / kT = \mu_j / (kT)$ . The Boltzmann constant defines the units in which the entropy is measured. By a change of units one can enforce any value of  $k$ . In traditional macroscopic units, the Boltzmann constant is very tiny

$$k \approx 1.38065 \cdot 10^{-23} J/K. \quad (8)$$



(For this and other constants, see CODATA [36]. In analogy with Planck's constant  $\hbar$ , we write  $\bar{k}$  in place of the customary  $k$  or  $k_B$ , in order to be free to use the letter  $k$  for other purposes.) Differentiation with respect to  $P$  shows that  $\Omega = V$  is the system size, and from (1), (3), and (15), we find that, in equilibrium,

$$P = \sum_j \pi_j(T) e^{\mu_j/\bar{k}T}, \quad S = V \sum_j \left( \frac{\partial}{\partial T} \pi_j(T) - \frac{\mu_j \pi_j(T)}{\bar{k}T^2} \right) e^{\mu_j/\bar{k}T},$$

$$N_j = \frac{V \pi_j(T)}{\bar{k}T} e^{\mu_j/\bar{k}T}, \quad H = V \sum_j \left( T \frac{\partial}{\partial T} \pi_j(T) - \pi_j(T) \right) e^{\mu_j/\bar{k}T}.$$

Expressed in terms of  $T, V, N$ , we have

$$PV = \bar{k}T \sum_j N_j, \quad \mu_j = \bar{k}T \log \frac{\bar{k}T N_j}{V \pi_j(T)},$$

$$H = \sum_j h_j(T) N_j, \quad h_j(T) = \bar{k}T \left( T \frac{\partial}{\partial T} \log \pi_j(T) - 1 \right),$$

from which  $S$  can be computed by means of the Euler equation (4). In particular, for one **mole** of a single substance, defined by  $N = R/\bar{k} \approx 6.02214 \cdot 10^{23}$  (the **Avogadro constant**), where  $R \approx 8.31447 \text{ J/K}$  is the **molar gas constant**, we get the **ideal gas law**

$$PV = RT; \tag{9}$$

cf. CLAPEYRON [33], JENSEN [66].

In general, the difference  $h_j(T) - h_j(T_0)$  can be found experimentally by measuring the energy needed for raising or lowering the temperature of pure substance  $j$  from  $T_0$  to  $T$  while keeping the  $N_j$  constant. In terms of infinitesimal increments, the **heat capacities**  $C_V(T) = dh_j(T)/dT$ , we have

$$h_j(T) = h_j(T_0) + \int_{T_0}^T dT C_V(T).$$

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

$$\pi_j(T) = \pi_j(T_0) \exp \int_{T_0}^T \frac{dT}{T} \left( 1 + \frac{h_j(T)}{\bar{k}T} \right).$$

Thus there are two undetermined integration constants for each particle species. These cannot be determined experimentally as long as we are in the range of validity of the ideal gas approximation. Indeed, if we pick arbitrary constants  $p_j$  and  $q_j$  and replace  $\pi_j(T), \mu_j, H$ , and  $S$  by

$$\pi'_j(T) := e^{p_j - q_j/\bar{k}T} \pi_j(T), \quad \mu'_j = \mu_j + q_j - \bar{k}T p_j,$$

$$H' = H + \sum_j p_j N_j, \quad S' = S + k \sum_j q_j N_j,$$

all relations remain unchanged. Thus, the Hamilton energy and the entropy of an ideal gas are only determined up to an arbitrary linear combination of the particle numbers. (This is an instance of the deeper problem to determine under which conditions thermodynamic variables are controllable; cf. the discussion in the context of Example 9.1 below.) In practice, this gauge freedom (present only in the ideal gas) can be fixed by choosing a particular **standard temperature**  $T_0$  and setting arbitrarily  $H_j(T_0) = 0$ ,  $\mu_j(T_0) = 0$ .

The ideal gas law (9) is the basis for the construction of gas thermometers, since 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 is proportional to  $L$ . Modern thermometers work along similar principles.

### 3 The laws of thermodynamics

To measure the temperature of a system, one brings it in thermal contact with a thermometer and waits until equilibrium is established. (**Thermal contact** is precisely the condition that this will happen in a short amount of time.) The system and the thermometer will have the same temperature, which can be read off the thermometer. If the system is much larger than the thermometer, this temperature will be essentially the same as the temperature of the system before the measurement. The possibility of measuring temperature is sometimes called the zeroth law of thermodynamics, following FOWLER & GUGGENHEIM [45]. For a survey of the problems involved in defining and measuring temperature outside equilibrium, see CASAS-VÁSQUEZ & JOU [29]. For the history of temperature, see ROLLER [113] and TRUESDELL [124].

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  $\alpha$  for  $P$  and  $\mu$  jointly.

**3.1 Definition.** A **state variable** is an almost everywhere continuously differentiable function  $\phi(T, \alpha)$  defined on the state space (or a 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

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

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

$$d\phi = \frac{\partial \phi}{\partial T} dT + \frac{\partial \phi}{\partial \alpha} \cdot d\alpha \tag{10}$$

describes the change of a state variable  $\phi$  under arbitrary (infinitesimal) reversible transformations. (Divide by  $d\lambda$  and recognize the chain rule! In formal mathematical terms, differentials are exact 1-forms on the state space manifold.)

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 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  $(\kappa, \lambda)$ ,

$$g(\kappa, \lambda) = g(T(\kappa, \lambda), \alpha(\kappa, \lambda)). \quad (11)$$

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 (11) with respect to  $\lambda$ ; it can be evaluated using (10), giving the **chain rule**

$$\left(\frac{\partial g}{\partial \lambda}\right)_\kappa = \frac{\partial g}{\partial T} \left(\frac{\partial T}{\partial \lambda}\right)_\kappa + \frac{\partial g}{\partial \alpha} \cdot \left(\frac{\partial \alpha}{\partial \lambda}\right)_\kappa. \quad (12)$$

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 (10), and simplifying using (3) gives the **Gibbs-Duhem equation**

$$0 = SdT - VdP + N \cdot d\mu \quad (13)$$

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

$$dH = TdS + SdT - PdV - VdP + \mu \cdot dN + N \cdot d\mu,$$

and using (13), this simplifies to the **first law of thermodynamics** (MAYER [86], JOULE citeJou, HELMHOLTZ citeHel, CLAUSIUS [34])

$$dH = TdS - PdV + \mu \cdot dN. \quad (14)$$

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 particle numbers, the entropy, and the Hamilton 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 (e.g., stars through radiation, fluids through the forces exerted by the container), 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; e.g., a heat bath to maintain constant temperature, or a potential well to account for the confinement in a container).

The result of this reduced description (for derivations, see, e.g., BALIAN [7], GRABERT [50], RAU & MÜLLER [105]) is a dynamical effect called **dissipation** (THOMSON [123]), described by the **second law of thermodynamics** (CLAUSIUS [35]). The Euler inequality (2) together with the Euler equation (4) only express the nondynamical part of the second law since, in equilibrium thermodynamics, dynamical questions are ignored: Axiom (ii) says that if  $S, V, N$  are conserved (thermal, mechanical and chemical isolation) then the **internal energy**,

$$U := TS - PV + \mu \cdot N \quad (15)$$

is minimal in equilibrium; if  $T, V, N$  are conserved (mechanical and chemical isolation of a system at constant temperature  $T$ ) then the **Helmholtz energy**,

$$A := U - TS = -PV + \mu \cdot N$$

is minimal in equilibrium; and if  $T, P, N$  are conserved (chemical isolation of a system at constant temperature  $T$  and pressure  $P$ ) then the **Gibbs energy**,

$$G := A + PV = \mu \cdot N$$

is minimal in equilibrium.

The **third law of thermodynamics** (NERNST [92]) says that entropy is nonnegative. This is a direct consequence of the monotonicity of  $\Delta(T, P, \mu)$  and (3).

**Consequences of the first law.** The first law of thermodynamics describes the observable energy balance in a reversible process. The total energy flux  $dH$  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 (13) 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, both equations together imply that  $d(TdS - PdV + \mu \cdot N - H)$  vanishes, which expresses the preservation of the Euler equation.

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

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

the **mechanical work**

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

and the **chemical work**

$$W_{\text{chem}} = \int \mu(\lambda) \cdot dN(\lambda)$$

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, since 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 particle numbers. In particular, in case of thermal, mechanical, or chemical **isolation**, the corresponding fluxes vanish identically. Thus, constant  $S$  characterizes thermally isolated, **adiabatic** systems, constant  $V$  characterizes mechanically isolated, **closed** systems, and constant  $N$  characterizes chemically isolated, **impermeable** systems. (The constancy depends on all properties of a standard system: global equilibrium, a single phase, and the absence of chemical reactions.) Of course, these boundary conditions are somewhat idealized situations, which, however, can be approximately realized in practice and are of immense scientific and technological importance. (Note that the terms 'closed system' has also a much more general interpretation – which we do *not* use in this paper –, namely as a conservative dynamical system.)

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

We see that the entropy and the volume behave just like the particle number. This analogy can be deepened by observing that particle 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" contained in a system<sup>2</sup>, since thermal energy flux is accompanied by

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<sup>2</sup>Thus, entropy is the modern replacement for the historical concepts of *phlogiston* and *caloric*, which failed to give a correct account of heat phenomena. Phlogiston turned out to be 'missing oxygen', an early analogue of the picture of positrons as holes, or 'missing electrons', 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

adding or removing heat. Looking at other extensive quantities, we also recognize energy as the natural measure of the amount of "power", momentum as the natural measure of the amount of "force", and mass as the natural measure of the amount of "inertia" 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".

**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 [22]), uncontrolled radiation, etc.. 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. In a purely kinematic setting as in our paper, 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. We derive here the extremal principles for the Hamilton energy, the Helmholtz energy, and the Gibbs energy<sup>3</sup>, which give rise to the **Hamilton potential**

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

the **Helmholtz potential**

$$A(T, V, N) := \max_{P, \mu} \{-PV + \mu \cdot N \mid \Delta(T, P, \mu) = 0; T > 0; P > 0\},$$

and the **Gibbs potential**

$$G(T, P, N) := \max_{\mu} \{\mu \cdot N \mid \Delta(T, P, \mu) = 0; T > 0; P > 0\}.$$

The Gibbs potential is of particular importance for everyday processes since the latter frequently happen at approximately constant temperature, pressure, and particle number. (For other thermodynamic potential used in practice, see ALBERTY [1]; for the maximum entropy principle, see Appendix B.)

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mechanical energy, thus discrediting the idea of heat being a substance. (For the precise relation of entropy and caloric, see KUHN [75, 76], WALTER [128], and the references quoted there.) In the modern picture, the extensivity of entropy models the substance-like properties of heat. But as there are no particles of space whose number is proportional to the volume, so there are no particles of heat whose number is proportional to the entropy.

<sup>3</sup>The different potentials are related by so-called Legendre transforms; cf. ROCKAFELLAR [112] for the mathematical properties of Legendre transforms, ARNOL'D [6] for their application in mechanics, and ALBERTY [1] for their application in chemistry.

### 3.2 Theorem. (Extremal principles)

(i) In an arbitrary state,

$$H \geq U(S, V, N), \quad (16)$$

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

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

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

(ii) In an arbitrary state,

$$H - TS \geq A(T, V, N), \quad (17)$$

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

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

$$H = A(T, V, N) + TS.$$

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

(iii) In an arbitrary state,

$$H - TS + PV \geq G(T, P, N), \quad (18)$$

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

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

$$H = G(T, P, N) + TS - PV.$$

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. (17) and the statement about equality is a direct consequence of Axiom 2.1(ii). Thus, the difference  $H - TS - A(T, V, N)$  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  $\mu$ , we note that for constant  $T$ , the first law (14) implies

$$dA = d(H - TS) = dH - TdS = -PdV + \mu \cdot dN.$$

For the reversible transformation which only changes  $P$  or  $\mu_j$ , we conclude that  $dA = -PdV$  and  $dA = \mu \cdot dN$ , respectively. Solving for  $P$  and  $\mu_j$ , respectively, implies the formulas for  $P$  and  $\mu_j$ .  $\square$

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 [107], PRAUSNITZ et al. [103]) or SAFT (CHAPMAN et al. [30, 31]).

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

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

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \quad (19)$$

$$A(T, \lambda V, \lambda N) = \lambda A(T, V, N), \quad (20)$$

$$G(T, P, \lambda N) = \lambda G(T, P, N), \quad (21)$$

$$U(\lambda^1 S^1 + \lambda^2 S^2, \lambda^1 V^1 + \lambda^2 V^2, \lambda^1 N^1 + \lambda^2 N^2) \leq \lambda^1 U(S^1, V^1, N^1) + \lambda^2 U(S^2, V^2, N^2), \quad (22)$$

$$A(T, \lambda^1 V^1 + \lambda^2 V^2, \lambda^1 N^1 + \lambda^2 N^2) \leq \lambda^1 A(T, V^1, N^1) + \lambda^2 A(T, V^2, N^2), \quad (23)$$

$$G(T, P, \lambda^1 N^1 + \lambda^2 N^2) \leq \lambda^1 G(T, P, N^1) + \lambda^2 G(T, P, N^2). \quad (24)$$

*In particular, these potentials are convex in  $S$ ,  $V$ , and  $N$ .*

*Proof.* The first three equations express homogeneity and are a direct consequence of the definitions. Inequality (23) holds since, for suitable  $P$  and  $\mu$ ,

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

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

For a system at constant temperature  $T$ , pressure  $P$ , and particle number  $N$ , consisting of a number of parts labeled by a superscript  $k$  which are separately in equilibrium, the Gibbs energy is extensive,

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

Equilibrium requires that  $\sum G^k$  is minimal among all choices with  $\sum N^k = N$ , and by introducing a Lagrange multiplier vector  $\mu^*$  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  $\mu^k$  must be the same. At constant  $T$ ,  $V$ , and  $N$ , one can do the same argument with the Helmholtz potential, and at constant  $S$ ,  $V$ , and  $N$  with the Hamilton potential. In each case, the equilibrium is characterized by the constancy of the intensive parameters.

Global equilibrium states are therefore macroscopically highly uniform. Their 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 [5], FORSTER [44]). In particular, the traditional interpretation of entropy as a measure of disorder is often misleading<sup>4</sup>: **Macroscopic disorder** is measured by the degree to which macroscopic space and time correlations are absent, *not* by entropy. In this sense, *global equilibrium states 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 do not exhaust all available macroscopic information. The global equilibrium state is a state without additional macroscopic information. The contents of the second law of thermodynamics for global equilibrium states may therefore be phrased as follows (cf. Appendix A): *At global equilibrium, macroscopic order (homogeneity) is perfect and microscopic complexity is maximal.*

Using only the present axioms, one can say something about the behavior of a system close to equilibrium, at least 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

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

so that  $dH/dt \leq 0$ . Assuming that the system is composed of two parts, both in equilibrium in the time interval between  $t$  and  $t^*$ , the time shift must be reversible on the parts, and the first law can be applied to them. Thus

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

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  $dH \leq 0$ , we find the inequality

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

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<sup>4</sup>Much more carefully argued support for this statement, with numerous examples from teaching practice, is in LAMBERT [77].

This 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 single species system at constant  $S^1$  and  $V^1$ , we have  $dN^1 \leq 0$  if  $\mu^1 > \mu^2$ ; i.e., "matter" (particle number) flows from higher chemical potential towards lower chemical potential. This gives temperature, pressure, and chemical potential the familiar intuitive interpretation.

This is a shadow of the far reaching fact that, in nonequilibrium thermodynamics, gradients in the intensive variables induce a dissipative dynamics that tends to diminish these gradients, thus enforcing (after the time needed to reach equilibrium) agreement of the intensive variables of different parts of a system. 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: heating to change the temperature, applying pressure to change the volume, immersion into a substance to change the chemical composition; also, in the more general thermal models discussed in Section 9 applying forces to displace an object, etc..

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

$$\delta E = H - U(S, V, N) = H - TS - A(S, V, N) = H - TS + PV = G(S, V, N)$$

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  $\delta E$  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.

The phenomenological description given so far is completely adequate for systems in global equilibrium with a single phase only and no chemical reactions. From the formulas provided, it is now an easy step to go to various examples and applications. A full discussion of global equilibrium would also involve the equilibrium treatment of multiple phases and chemical reactions. However, these involve no foundational problems, and their discussion would

offer little new compared with traditional textbook treatments. Hence they are not treated here.

More important is the observation that, when considered in sufficient detail, no physical system is truly in global equilibrium; one can always find smaller or larger deviations. To describe these deviations, extra variables are needed, resulting in a more complete but also more complex model. At even higher resolution, this model is again imperfect and an approximation to an even more complex, better model. This refinement process may be repeated in many, perhaps even infinitely many stages. At the most detailed stages, we transcend the frontier of current knowledge in physics, but even as this frontier recedes, deeper and deeper stages with unknown details are imaginable.

Therefore, it is desirable to have a meta-description of thermodynamics that, starting with a detailed model, allows to deduce the properties of each coarser model, in a way that all description levels are consistent with the current state of the art in physics. Moreover, the results should be as independent as possible of unknown details at the lowest levels.

This will be done in the remainder of the paper. First we'll look at an anonymous bottom level, where Gibbs states are the players in the field and define values for arbitrary quantities. As in this section, the intensive variables determine the state (which now is a more abstract object), whereas the extensive variables now appear as values of other abstract objects called quantities. This change of setting allows the natural incorporation of quantum mechanics, where quantities need not commute, while values are numbers observable in principle, hence must satisfy the commutative law.

Then we introduce thermal states by selecting the quantities whose values shall act as extensive variables in a thermal model. On this level, we shall be able to reproduce the phenomenological setting of the present section from first principles; see the discussion after Theorem 8.3. If the underlying detailed model is assumed to be known then the system function, and with it all thermal properties, are computable in principle, although we only hint at the ways to do this numerically. We also look at a hierarchy of thermal models based on the same bottom level description and discuss how to decide which description levels are appropriate.

## 4 Gibbs states

Any fundamental description of physical systems must give account of the numerical values of quantities observable in experiments when the system under consideration is in a specified state. Moreover, the form and meaning of states, and what is observable in principle, must be clearly defined. For reasons given in NEUMAIER [93], we avoid using the customary word 'observable', and consider an axiomatic conceptual foundation on the basis of quantities and their values. This is consistent with the conventions adopted by the International System

of Units (SI) [120], who declare: "A quantity in the general sense is a property ascribed to phenomena, bodies, or substances that can be quantified for, or assigned to, a particular phenomenon, body, or substance. [...] The value of a physical quantity is the quantitative expression of a particular physical quantity as the product of a number and a unit, the number being its numerical value." Since quantities can be added and multiplied, the set of all quantities has an algebraic structure whose properties we now formulate.

The **quantities** of interest are taken to be the elements of a **Euclidean \*-algebra**  $\mathbb{E}$ . The simplest family of Euclidean \*-algebras, and the only one with which the reader must be familiar to understand the paper, is the algebra  $\mathbb{E} = \mathbb{C}^{N \times N}$  of square complex  $N \times N$  matrices. (This algebra models an N-level quantum system, but also quantum field theory in the lattice approximation.) Here the quantities are square matrices, the constants are the multiples of the identity matrix, involution  $*$  is conjugate transposition, and the integral  $\int$  is the trace, so that all quantities are strongly integrable.

For those, who want to understand a little more, we give a formally precise definition. To say that a set  $\mathbb{E}$  of quantities is a Euclidean \*-algebra means the following:  $\mathbb{E}$  is a complex vector space containing the complex numbers as **constants**. Apart from an associative product (commutative only in the classical case) one has an **involution**  $*$  reducing on the constants to complex conjugation and a complex-valued **integral**  $\int$  defined on a subspace of **strongly integrable** quantities. (The integral can often be naturally extended to a significantly larger class of integrable quantities.) A **partial order**  $\geq$  is then defined by  $g \geq 0$  iff  $g^* = g$  and  $\int h^* g h \geq 0$  for all strongly integrable  $h$ , and  $g \geq h$  iff  $g - h \geq 0$ . A quantity  $g$  is called **Hermitian** if  $g^* = g$ , and **bounded** if  $g^* g \leq \alpha^2$  for some  $\alpha \in \mathbb{R}$ . Apart from the standard rules for \*-algebras (NEUMAIER [93] discusses in detail what must be assumed and what can then be proved) and the linearity of the integral, we assume the following axioms for all bounded quantities  $g, h$  and all strongly integrable  $h_l$ :

- (EA1)  $g$  bounded,  $h$  strongly integrable  $\Rightarrow h^*, gh, hg$  strongly integrable,
- (EA2)  $(\int h)^* = \int h^*, \int gh = \int hg$ ,
- (EA3)  $\int h^* h > 0$  if  $h \neq 0$ ,
- (EA4)  $\int h^* g h = 0$  for all strongly integrable  $h \Rightarrow g = 0$  (**nondegeneracy**),
- (EA5)  $\int h_l^* h_l \rightarrow 0 \Rightarrow \int g h_l \rightarrow 0, \int h_l^* g h_l \rightarrow 0$ ,
- (EA6)  $h_l \downarrow 0 \Rightarrow \inf \int h_l = 0$  (**Dini property**).

Here, integrals extend over the longest following product or quotient (while later, differential operators act on the shortest syntactically meaningful term), the monotonic limit is defined by  $g_l \downarrow 0$  iff, for every strongly integrable  $h$ , the sequence (or net)  $\int h^* g_l h$  consists of real numbers converging monotonically decreasing to zero. The reader is invited to check explicitly that (EA1)–(EA6) hold for  $\mathbb{E} = \mathbb{C}^{N \times N}$ .

Note that (EA3) implies the Cauchy-Schwarz inequality

$$\int (gh)^*(gh) \leq \int g^* g \int h^* h,$$

which implies that every strongly integrable quantity is bounded. Some results needed in

the following are given in Appendix C, but proved there only in case  $\mathbb{E}$  is finite-dimensional. To justify our treatment rigorously in case the algebra  $\mathbb{E}$  is infinite-dimensional, one would need to use (EA5) and (EA6) and perhaps further, technical assumptions. However, the main text is fully rigorous if the results of Appendix C are assumed in addition to (EA1)–(EA6).

**4.1 Examples.** Apart from the matrix algebra, three basic realizations of the axioms are relevant to nonrelativistic physics. We give here some details to draw the connection with traditional statistical mechanics. However, the remainder is completely independent of details how our axioms are realized; a specific realization is needed only when doing specific quantitative calculations. Therefore, the reader lacking the formal mathematical background to understand some details in these examples may simply skip them.

(i) **(Nonrelativistic classical mechanics)** An atomic  $N$ -particle system is described in classical mechanics by the phase space  $\mathbb{R}^{6N}$  with six coordinates – position  $x^a \in \mathbb{R}^3$  and momentum  $p^a \in \mathbb{R}^3$  – for each particle.) The algebra

$$\mathbb{E}_N := C^\infty(\mathbb{R}^{6N})$$

of infinitely differentiable, complex-valued functions  $g(x^{1:N}, p^{1:N})$  of positions and momenta is a Euclidean  $*$ -algebra with complex conjugation as involution and the **Liouville integral**

$$\int g = C^{-1} \int dp^{1:N} dx^{1:N} g_N(x^{1:N}, p^{1:N}),$$

where  $C$  is a positive constant. Strongly integrable quantities are the Schwartz functions in  $\mathbb{E}$ . The axioms are easily verified.

(ii) **(Classical fluids)** A fluid is classically described by an atomic system with an indefinite number of particles. The appropriate algebra for a single species of monatomic particles is the direct sum  $\mathbb{E} = \bigoplus_{N \geq 0} \mathbb{E}_N$  whose quantities are infinite sequences  $g = (g_0, g_1, \dots)$  of  $g_N \in \mathbb{E}_N$ , with  $\mathbb{E}_N$  as in (i), and weighted Liouville integral

$$\int g = \sum_{N \geq 0} C_N^{-1} \int dp^{1:N} dx^{1:N} g_N(x^{1:N}, p^{1:N}).$$

Here  $C_N$  is a symmetry factor for the symmetry group of the  $N$ -particle system, which equals  $h^{3N} N!$  for indistinguishable particles;  $h = 2\pi\hbar$  is Planck's constant. This accounts for the Maxwell statistics and gives the correct entropy of mixing. Classical fluids with monatomic particles of several different kinds requires a tensor product of several such algebras, and classical fluids composed of molecules requires additional degrees of freedom to account for the rotation and vibration of the molecules.

(iii) **(Nonrelativistic quantum mechanics)** Let  $\mathbb{H}$  be a Euclidean space, a dense subspace of a Hilbert space. Then the algebra  $\mathbb{E} := \text{Lin } \mathbb{H}$  of continuous linear operators on  $\mathbb{H}$  is a Euclidean  $*$ -algebra with the adjoint as involution and the **quantum integral**

$$\int g = \text{tr } g,$$

given by the trace of the quantity in the integrand. Strongly integrable quantities are the operators  $g \in \mathbb{E}$  for which all  $hgh'$  with  $h, h' \in \mathbb{E}$  are trace class. (This includes all linear operators of finite rank.) Again, the axioms are easily verified.

Our next task is to specify the formal properties of the value of a quantity. We assign to certain quantities  $g$  (including all bounded quantities) a **value**  $\langle g \rangle$ . Such an assignment is called a **state** (of the system under investigation) if it has the following properties (of which we only use the first three explicitly; the fourth would be needed to justify certain operations involving differentiation, which we silently assume to be valid):

- (R1)  $\langle 1 \rangle = 1$ ,  $\langle g^* \rangle = \langle g \rangle^*$ ,  $\langle g + h \rangle = \langle g \rangle + \langle h \rangle$ ,
- (R2)  $\langle \alpha g \rangle = \alpha \langle g \rangle$  for  $\alpha \in \mathbb{C}$ ,
- (R3) If  $g \geq 0$  then  $\langle g \rangle \geq 0$ ,
- (R4) If  $g_l \in \mathbb{E}$ ,  $g_l \downarrow 0$  then  $\inf_l \langle g_l \rangle = 0$ .

Note that this formal definition of a state – always used in the remainder of the paper – differs from the phenomenological version in Section 2. The connection will be made in Section 8.

In practice, states are assigned by well-informed and experimentally testable judgment concerning one’s equipment. Indeed, from a practical point of view, *theory defines what an object is*: A gas is considered to be an ideal gas with certain values of temperature, pressure and volume if it behaves to a satisfactory degree like the mathematical model of an ideal gas with these parameters, and a solid is considered to be a crystal with certain numerical properties if it behaves to a satisfactory degree like the mathematical model of a crystal with these properties<sup>5</sup>. In general, we know (or rather assume on the basis of past experience, claims of manufacturers, etc.) that certain materials or machines reliably produce states that (to a satisfactory degree for the purpose of the experiment or application) depend only on variables that are accounted for in our theory and that are, to a satisfactory degree, either fixed or controllable. The nominal state of a system can be checked and, if necessary, corrected by **calibration**, using appropriate measurements which reveal the parameters characterizing the state.

All states arising in thermodynamics have the following particular form.

**4.2 Definition.** A **Gibbs state** is defined by the values

$$\langle g \rangle := \int e^{-S/\kappa} g, \tag{25}$$

where  $S$ , called the **entropy** of the state, is a Hermitian quantity with strongly integrable  $e^{-S/\kappa}$ , satisfying the normalization condition

$$\int e^{-S/\kappa} = 1, \tag{26}$$

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<sup>5</sup> cf. CALLEN [26, p.15]: “Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory.”

and  $k$  is the Boltzmann constant (8). The special case  $f = S/k$ ,  $Z = 1$  of Theorem 4.3 below implies that a Gibbs state is indeed a state.

What is traditionally (and in Section 2) called entropy and denoted by  $S$  is in the present setting the value  $\overline{S} = \langle S \rangle$ . What is here called entropy, has in the literature on statistical mechanics a variety of alternative names. For example, GIBBS [48] (who first noticed the rich thermodynamic implications of states defined by (25)) called  $-S$  the *index of probability*; ALHASSID & LEVINE [3] and BALIAN [8] use the name *surprisal* for  $S$ . Our terminology is close to that of MRUGALA et al. [89], who call  $S$  the *microscopic entropy*, and HASSAN et al. [58], who call  $S$  the *information(al) entropy operator*.

### 4.3 Theorem.

(i) A Gibbs state determines its entropy uniquely.

(ii) For any Hermitian quantity  $f$  with strongly integrable  $e^{-f}$ , the mapping  $\langle \cdot \rangle_f$  defined by

$$\langle g \rangle_f := Z^{-1} \int e^{-f} g, \quad Z := \int e^{-f} \quad (27)$$

is a state. It is a Gibbs state with entropy

$$S := k(f + \log Z). \quad (28)$$

(iii) The **KMS condition** (cf. KUBO [73], MARTIN & SCHWINGER [83])

$$\langle gh \rangle_f = \langle h Q_f g \rangle \quad \text{for bounded } g, h \quad (29)$$

holds. Here  $Q_f$  is the linear mapping defined by

$$Q_f g := e^{-f} g e^f.$$

*Proof.* (i) If the entropies  $S$  and  $S'$  define the same Gibbs state then

$$\int (e^{-S/k} - e^{-S'/k}) g = \langle g \rangle - \langle g \rangle = 0$$

for all  $g$ , hence  $e^{-S/k} - e^{-S'/k} = 0$ . This implies that  $e^{-S/k} = e^{-S'/k}$ , hence  $S = S'$  by Proposition C.1.

(ii) The quantity  $d := e^{-f/2}$  is nonzero and satisfies  $d^* = d$ ,  $e^{-f} = d^* d \geq 0$ . Hence  $Z > 0$  by (EA3), and  $\rho := Z^{-1} e^{-f}$  is Hermitian and nonnegative. For  $h \geq 0$ , the quantity  $g = \sqrt{f}$  is Hermitian (by Proposition C.1) and satisfies  $g \rho g^* = Z^{-1} (gd)(gd)^* \geq 0$ , hence by (EA2),

$$\langle h \rangle_f = \langle g^* g \rangle_f = \int \rho g^* g = \int g \rho g^* \geq 0.$$

Moreover,  $\langle 1 \rangle_f = Z^{-1} \int e^{-f} = 1$ . Similarly, if  $g \geq 0$  then  $g = h^* H$  with  $h = \sqrt{g} = h^*$  and with  $k := e^{-f/2} h$ , we get

$$Z \langle g \rangle_f = \int e^{-f} h h^* = \int h^* e^{-f} h = \int k^* k \geq 0.$$

This implies (R3). the other axioms (R1)–(R4) follow easily from the corresponding properties of the integral. Thus  $\langle \cdot \rangle_f$  is a state. Finally, with the definition (28), we have

$$Z^{-1}e^{-f} = e^{-f - \log Z} = e^{-S/k},$$

whence  $\langle \cdot \rangle_f$  is a Gibbs state.

(iii) By (EA2),  $\langle hQ_f g \rangle_f = \int e^{-f} h Q_f g = \int Q_f g e^{-f} h = \int e^{-f} g h = \langle g h \rangle_f$ . □

Note that the state (27) is unaltered when  $f$  is shifted by a constant.  $Q_f$  is called the **modular automorphism** of the state  $\langle \cdot \rangle_f$  since  $Q_f(gh) = Q_f(g)Q_f(h)$ ; for a classical system,  $Q_f$  is the identity. In the following, we shall not make use of the KMS condition; however, it plays an important role in the mathematics of the thermodynamic limit (cf. THIRRING [122]).

We call  $Z$  the **partition function** of  $f$ ; it is a function of whatever parameters appear in a particular form given to  $f$  in the applications. A large part of traditional statistical mechanics is concerned with the calculation of the partition function  $Z$  and of special values when  $f$  is given. As we shall see, much of the qualitative theory of statistical mechanics is completely independent of the details involved, and it is this part that we concentrate upon in this paper.

**4.4 Example.** A **canonical ensemble**<sup>6</sup>, is defined as a Gibbs state whose entropy is an affine function of a Hermitian quantity  $H$ , called the **Hamiltonian**:

$$S = \beta H + \text{const},$$

with a constant depending on  $\beta$ , computable from (28) and the partition function

$$Z = \int e^{-\beta H}$$

of  $f = \beta H$ . In particular, if  $S$  is quantized then, in order that  $Z$  is finite,  $S$  and hence  $H$  must have a discrete spectrum that is bounded below, and the partition function takes the familiar form

$$Z = \text{tr } e^{-\beta H} = \sum_{n \in \mathcal{N}} e^{-\beta E_n}, \tag{30}$$

where the  $E_n$  ( $n \in \mathcal{N}$ ) are the **energy levels**, the eigenvalues of  $H$ . If the spectrum of  $H$  is known, this leads to explicit formulas for  $Z$ . For example, a **two level system** is defined by the energy levels  $0, E$  (or  $E_0$  and  $E_0 + E$ , which gives the same results), and has

$$Z = 1 + e^{-\beta E}. \tag{31}$$

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<sup>6</sup> This traditional terminology appears to be unalterably fixed. We shall therefore use the term **ensemble** interchangeable with state. However, we want to stress that, in the present setting, an ensemble may consist of a single system only, rather than – as in the traditional statistical interpretation – of a large collection of identically prepared systems. The latter interpretation has well-known difficulties to explain why each single macroscopic system is described correctly by thermodynamics.



It describes a single **Fermion mode**, but also many other systems at low temperature; cf. (109). In particular, it is the basis of laser-induced chemical reactions in photochemistry (see, e.g., KARLOV [68], MUROV et al. [91]), where only two molecular energy levels are activated.

For a **harmonic oscillator**, defined by the energy levels  $nE$ ,  $n = 0, 1, 2, \dots$  and describing a single **Boson mode**, we have

$$Z = \sum_{n=0}^{\infty} e^{-n\beta E} = (1 - e^{-\beta E})^{-1}.$$

Independent modes are modelled by taking tensor products of single mode algebras and adding their Hamiltonians, leading to spectra which are obtained by summing the eigenvalues of the modes in all possible ways. The resulting partition function is the product of the single-mode partition functions. From here, a thermodynamic limit leads to the properties of ideal gases. Then nonideal gases due to interactions can be handled using the cumulant expansion, as indicated at the end of this section. The details are outside the scope of this paper.

Since the Hamiltonian can be any Hermitian quantity, the quantum partition function formula (30) can in principle be used to compute the partition function of arbitrary quantized Hermitian quantities.

## 5 Kubo product and generating functional

The negative logarithm of the partition function, the so-called generating functional, plays a fundamental role in the foundation of thermodynamics.

We first discuss a number of general properties, discovered by GIBBS [48], PEIERLS [98], BOGOLIUBOV [19], KUBO [74], MORI [88], and GRIFFITHS [53]. The somewhat technical setting involving the Kubo inner product is necessary to handle noncommuting quantities correctly; everything would be much easier in the classical case.

But the reader can be assured that (together with Appendix C) this section is the only technical part of the paper, and the effort in understanding what goes on is more than compensated for by the ease with which everything else follows. On a first reading, the proofs in this section may simply be skipped.

**5.1 Proposition.** *Let  $f$  be Hermitian such that  $e^{sf}$  is strongly integrable for all  $s \in [-1, 1]$ . Then*

$$\langle g; h \rangle_f := \langle gE_f h \rangle_f, \tag{32}$$

where  $E_f$  is the linear mapping defined for Hermitian  $f$  by

$$E_f g := \int_0^1 ds e^{-sf} g e^{sf},$$

defines a bilinear, positive definite inner product  $\langle \cdot; \cdot \rangle_f$  on the algebra of quantities, called the **Kubo** (or **Mori** or **Bogoliubov**) **inner product**. For all  $f, g$ , the following relations hold:

$$\langle g; h \rangle_f^* = \langle h^*; g^* \rangle_f. \quad (33)$$

$$\langle g^*; g \rangle_f > 0 \quad \text{if } g \neq 0. \quad (34)$$

$$\langle g; h \rangle_f = g \langle h \rangle_f \quad \text{if } g \in \mathbb{C}, \quad (35)$$

$$\langle g; h \rangle_f = \langle gh \rangle_f \quad \text{if } g \text{ or } h \text{ commutes with } f, \quad (36)$$

$$E_f g = g \quad \text{if } g \text{ commutes with } f, \quad (37)$$

If  $f = f(\lambda)$  depends continuously differentiably on the real parameter vector  $\lambda$  then

$$\frac{d}{d\lambda} e^{-f} = - \left( E_f \frac{df}{d\lambda} \right) e^{-f}. \quad (38)$$

*Proof.* (i) We have

$$\langle g; h \rangle_f^* = \langle (g E_f h)^* \rangle_f = \langle (E_f h)^* g^* \rangle_f = \left\langle \int_0^1 ds e^{sf} h^* e^{-sf} g^* \right\rangle_f = \int_0^1 ds \langle e^{sf} h^* e^{-sf} g^* \rangle_f.$$

The integrand equals

$$\int e^{-f} e^{sf} h^* e^{-sf} g^* = \int e^{sf} e^{-f} h^* e^{-sf} g^* = \int e^{-f} h^* e^{-sf} g^* e^{sf} = \langle h^* e^{-sf} g^* e^{sf} \rangle_f$$

by (EA2), hence

$$\langle g; h \rangle_f^* = \int_0^1 ds \langle h^* e^{-sf} g^* e^{sf} \rangle_f = \left\langle h^* \int_0^1 ds e^{-sf} g^* e^{sf} \right\rangle_f = \langle h^* E_f g^* \rangle_f = \langle h^*; g^* \rangle_f.$$

Thus (33) holds.

(ii) Suppose that  $g \neq 0$ . For  $s \in [0, 1]$ , we define  $u = s/2, v = (1-s)/2$  and  $g(s) := e^{-uf} g e^{vf}$ . Since  $f$  is Hermitian,  $g(s)^* = e^{vf} g^* e^{-uf}$ , hence by (EA2) and (EA3),

$$\int e^{-f} g^* e^{-sf} g e^{sf} = \int e^{vf} g e^{-2uf} g^* e^{vf} = \int g(s)^* g(s) > 0,$$

so that

$$\langle g^*; g \rangle_f = \langle g^* E_f g \rangle_f = \int_0^1 ds \int e^{-f} g^* e^{-sf} g e^{sf} > 0.$$

This proves (34), and shows that the Kubo inner product is positive definite.

(iii) If  $f$  and  $g$  commute then  $ge^{sf} = e^{sf}g$ , hence

$$E_f g = \int_0^1 ds e^{-sf} e^{sf} g = \int_0^1 ds g = g,$$

giving (37). The definition of the Kubo inner product then implies (36), and taking  $g \in \mathbb{C}$  gives (35).

(iv) The function  $q$  on  $[0, 1]$  defined by

$$q(t) := \int_0^t ds e^{-sf} \frac{df}{d\lambda} e^{sf} + \left( \frac{d}{d\lambda} e^{-tf} \right) e^{tf}$$

satisfies  $q(0) = 0$  and

$$\frac{d}{dt} q(t) = e^{-tf} \frac{df}{d\lambda} e^{tf} + \left( \frac{d}{d\lambda} e^{-tf} \right) f e^{tf} + \frac{d}{d\lambda} (-e^{-tf} f) e^{tf} = 0.$$

Hence  $q$  vanishes identically. In particular,  $q(1) = 0$ , giving (38).  $\square$

As customary in thermodynamics, we use differentials to express relations involving the differentiation by arbitrary parameters. To write (38) in differential form, we formally multiply by  $d\lambda$ , and obtain the **quantum chain rule** for exponentials,

$$de^{-f} = (-E_f df) e^{-f}. \quad (39)$$

If the  $f(\lambda)$  commute for all values of  $\lambda$  then the quantum chain rule reduces to the classical chain rule. Indeed, then  $f$  commutes also with  $\frac{df}{d\lambda}$ ; hence  $E_f \frac{df}{d\lambda} = \frac{df}{d\lambda}$ , and  $E_f df = df$ .

*The following theorem is central to the mathematics of thermodynamics.* As will be apparent from the subsequent discussion, part (i) is the abstract mathematical form of the second law of thermodynamics, part (iii) is the abstract form of the first law, and part (ii) allows the actual computation of thermal properties from microscopic assumptions.

**5.2 Theorem.** *Let  $f$  be Hermitian such that  $e^{sf}$  is strongly integrable for all  $s \in [-1, 1]$ .*

(i) **The generating functional**

$$W(f) := -\log \int e^{-f} \quad (40)$$

*is a concave function of the Hermitian quantity  $f$ . In particular,*

$$W(g) \leq W(f) + \langle g - f \rangle_f. \quad \text{(Gibbs-Bogoliubov inequality)} \quad (41)$$

*Equality holds in (41) iff  $f$  and  $g$  differ by a constant.*

(ii) For Hermitian  $g$ , the **cumulant expansion**

$$W(f + \tau g) = W(f) + \tau \langle g \rangle_f - \frac{\tau^2}{2} (\langle g \rangle_f^2 - \langle g; g \rangle_f) + O(\tau^3) \quad (42)$$

holds if the coefficients are finite.

(iii) If  $f = f(\lambda)$  and  $g = g(\lambda)$  depend continuously differentiably on  $\lambda$  then the following **differentiation formulas** hold:

$$d\langle g \rangle_f = \langle dg \rangle_f - \langle g; df \rangle_f + \langle g \rangle_f \langle df \rangle_f, \quad (43)$$

$$dW(f) = \langle df \rangle_f. \quad (44)$$

(iv) The entropy of the state  $\langle \cdot \rangle_f$  is

$$S = k(f - W(f)). \quad (45)$$

*Proof.* We prove the assertions in reverse order.

(iv) Equation (40) says that  $W(f) = -\log Z$ , which together with (28) gives (45).

(iii) We have

$$\begin{aligned} df g e^{-f} &= \int d g e^{-f} + \int g d e^{-f} = \int d g e^{-f} - \int g E_f d f e^{-f} \\ &= \int (d g - g E_f d f) e^{-f} = Z \langle d g - g E_f d f \rangle_f. \end{aligned}$$

On the other hand,  $d \int g e^{-f} = d(Z \langle g \rangle_f) = dZ \langle g \rangle_f + Z d\langle g \rangle_f$ , so that

$$dZ \langle g \rangle_f + Z d\langle g \rangle_f = Z \langle d g - g E_f d f \rangle_f = Z \langle d g \rangle_f - Z \langle g; d f \rangle_f. \quad (46)$$

In particular, for  $g = 1$  we find by (35) that  $dZ = -Z \langle 1; d f \rangle_f = -Z \langle d f \rangle_f$ . Now (44) follows from  $dW(f) = -d \log Z = -dZ/Z = \langle d f \rangle_f$ , and solving (46) for  $d\langle g \rangle_f$  gives (43).

(ii) We introduce the function  $\phi$  defined by

$$\phi(\tau) := W(f + \tau g),$$

From (44), we find  $\phi'(\tau) = \langle g \rangle_{f+\tau g}$  for  $f, g$  independent of  $\tau$ , and by differentiating this again,

$$\phi''(\tau) = \frac{d}{d\tau} \langle g \rangle_{f+\tau g} = - \left\langle g \frac{E_f d(f + \tau g)}{d\tau} \right\rangle_{f+\tau g} + \langle g \rangle_{f+\tau g}^2.$$

In particular,

$$\phi'(0) = \langle g \rangle_f, \quad \phi''(0) = \langle g \rangle_f^2 - \langle g E_f g \rangle_f = \langle g \rangle_f^2 - \langle g; g \rangle_f. \quad (47)$$

A Taylor expansion now implies (42).

(i) Since the Cauchy-Schwarz equation for the Kubo inner product implies

$$\langle g \rangle_f^2 = \langle g; 1 \rangle_f^2 \leq \langle g; g \rangle_f \langle 1; 1 \rangle_f = \langle g; g \rangle_f,$$

we see that

$$\left. \frac{d^2}{d\tau^2} W(f + \tau g) \right|_{\tau=0} \leq 0$$

for all  $f, g$ . This implies that  $W(f)$  is concave. Moreover, replacing  $f$  by  $f + sg$ , we find that  $\phi''(s) \leq 0$  for all  $s$ . The remainder form of Taylor's theorem therefore gives

$$\phi(\tau) = \phi(0) + \tau\phi'(0) + \int_0^\tau ds(\tau - s)\phi''(s) \leq \phi(0) + \tau\phi'(0),$$

and for  $\tau = 1$  we get

$$W(f + g) \leq W(f) + \langle g \rangle_f. \quad (48)$$

(41) follows for  $\tau = 1$  upon replacing  $g$  by  $g - f$ .

By the derivation, equality holds in (48) only if  $\phi''(s) = 0$  for all  $0 < s < 1$ . By (47), applied with  $f + sg$  in place of  $f$ , this implies  $\langle g \rangle_{f+sg}^2 = \langle g; g \rangle_{f+sg}$ . Thus we have equality in the Cauchy-Schwarz argument, forcing  $g$  to be a multiple of 1. Therefore equality in the Gibbs-Bogoliubov inequality (41) is possible only if  $g - f$  is a constant.  $\square$

**5.3 Theorem.** *Let  $S_c$  be the entropy of a reference state. Then, for an arbitrary Gibbs state  $\langle \cdot \rangle$  with entropy  $S$ ,*

$$\langle S \rangle \leq \langle S_c \rangle, \quad (49)$$

*with equality only if  $S_c = S$ .*

*Proof.* Let  $f = S/k$  and  $g = S_c/k$ . Since  $S$  and  $S_c$  are entropies,  $W(f) = W(g) = 0$ , and the Gibbs-Bogoliubov inequality (41) gives  $0 \leq \langle g - f \rangle_f = \langle S_c - S \rangle/k$ . This implies (49). If equality holds then equality holds in (41), so that  $S_c$  and  $S$  differ only by a constant. But this constant vanishes since the values agree.  $\square$

The difference

$$\langle S_c - S \rangle = \langle S_c \rangle - \langle S \rangle \geq 0 \quad (50)$$

is known as **relative entropy**. It can be interpreted as the amount of information in a state  $\langle \cdot \rangle$  which cannot be explained by the reference state. This interpretation makes sense since the relative entropy vanishes precisely for the reference state. A large relative entropy therefore indicates that the state contains some important information not present in the reference state.

**Approximations.** The cumulant expansion is the basis of a well-known approximation method in statistical mechanics. Starting from special reference states  $\langle \cdot \rangle_f$  with explicitly

known  $W(f)$  and  $E_f$  (corresponding to so-called explicitly solvable models), one obtains inductively expressions for values in these states by applying the differentiation rules. (In the most important cases, the resulting formulas for the values are commonly referred to as a **Wick theorem**, cf. WICK [131]. For details, see textbooks on statistical mechanics, e.g., HUANG [61], REICHL [106].)

From these, one can calculate the coefficients in the cumulant expansion; note that higher order terms can be found by proceeding as in the proof, using further differentiation. This gives approximate generating functions (and by differentiation associated values) for Gibbs states with an entropy close to the explicitly solvable reference state. From the resulting generating function and the differentiation formulas (43)–(44), one gets as before the values for the given state.

The best reference state  $\langle \cdot \rangle_f$  to use for a given Gibbs state  $\langle \cdot \rangle_g$  can be obtained by minimizing the upper bound in the Gibbs-Bogoliubov inequality (41) over the  $f$  for which an explicit generating function is known. Frequently, one simply approximates  $W(g)$  by the minimum of this upper bound,

$$W(g) \approx W_m(g) := \inf_f \left( W(f) + \langle g - f \rangle_f \right). \quad (51)$$

Using  $W_m(g)$  in place of  $W(g)$  defines a so-called **mean field theory**; cf. CALLEN [26]. For computations from first principles (quantum field theory), see, e.g., the survey by BERGES et al. [15].

## 6 Limit resolution and statistics

In statistical mechanics, our values of quantities are called expectations, and refer to the mean over an ensemble of (real or imagined) identically prepared systems. While we keep the notation with pointed brackets familiar from statistical mechanics, we want to avoid any probabilistic connotation, hence use our more neutral term *vthat* does not require a statistical interpretation.

We now discuss in which sense the interpretation of the values of quantities as objective, observer-independent properties is valid. The key is an analysis of the uncertainty inherent in the description of a system by a state, based on the following result. (Cf. NEUMAIER [93] for a preliminary version of this interpretation.)

**6.1 Proposition.** *For Hermitian  $g$ ,*

$$\langle g \rangle^2 \leq \langle g^2 \rangle. \quad (52)$$

*Equality holds if  $g = \langle g \rangle$ .*

*Proof.* Put  $\bar{g} = \langle g \rangle$ . Then  $0 \leq \langle (g - \bar{g})^2 \rangle = \langle g^2 - 2\bar{g}g + \bar{g}^2 \rangle = \langle g^2 \rangle - 2\bar{g}\langle g \rangle + \bar{g}^2 = \langle g^2 \rangle - \langle g \rangle^2$ . This gives (52). If  $g = \bar{g}$  then equality holds in this argument.  $\square$

As a consequence, we can define the **limit resolution**

$$\text{Res}(g) := \sqrt{\langle g^2 \rangle / \langle g \rangle^2 - 1}, \quad (53)$$

of a Hermitian quantity  $g$  with nonzero value  $\langle g \rangle$ , an uncertainty measure specifying how accurately one can treat  $g$  as a sharp number, given by this value.

In experimental practice, the limit resolution is a lower bound on the relative accuracy with which one can expect  $\langle g \rangle$  to be determinable reliably<sup>7</sup> from measurements of a single system at a single time. In particular, a quantity  $g$  is considered to be **significant** if  $\text{Res}(g) \ll 1$ , while it is **noise** if  $\text{Res}(g) \gg 1$ . If  $g$  is a quantity and  $\tilde{g}$  is a good approximation of its value then  $\varepsilon := g - \tilde{g}$  is noise.

For a single system at a single time, values  $\langle g \rangle$  have in intermediate cases, where  $\text{Res}(g)$  has the order of unity, no experimentally testable meaning. However, time averages of  $\bar{g}(t_i)$  at different times  $t_i$  may have a meaning – they are the values of the quantity  $\tilde{g}$  defined as the average of the  $g(t_i)$ , and by the law of large numbers, this quantity may be significant even if each single  $g(t_i)$  is not.

Thus, this terminology captures correctly the experimental practice, without imposing any statistical or probabilistic connotations. On the contrary, it determines the precise conditions under which statistical reasoning is justified.

**Objective probability.** The exposition in WHITTLE [130] (or, in more abstract terms, already GELFAND & NAIMARK [47]) shows that, if  $H$  and the  $X_j$  are pairwise commuting, there is a way consistent with the traditional axioms for probability theory (as formalized by KOLMOGOROV [71]) to define, for any Gibbs state in our sense, random variables  $H$  and  $X_j$  such that the expectation of all sufficiently regular functions  $f(H, X)$  defined on the joint spectrum of  $(H, X)$  agrees with the value of  $f$ . Thus, in the pairwise commuting case, it is always possible to construct a probability interpretation for the quantities, *completely independent of any assumed microscopic reality*.

However, if – as in quantum systems – the extensive quantities do not commute, a probabilistic interpretation in the traditional Kolmogorov sense is no longer possible. Insisting in the quantum case on a probabilistic interpretation brings with it the well-known difficulties of quantum philosophy for systems which cannot be repeatedly prepared. It is gratifying that the present setting avoids these difficulties in an elegant way: There is no need at all to

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<sup>7</sup>The situation is analogous to the limit resolution with which one can determine the longitude and latitude of a city such as Vienna. Clearly these are well-defined only up to some limit resolution defined by the diameter of the city.

introduce probabilities into the description; everything applies to the single system under study.

**Subjective probability.** Our formalism is closely related to that used in statistics for random phenomena expressible in terms of exponential families; cf. Remark 7.2(v) below. In such a context, a Bayesian, subjective probability interpretation (see, e.g., BARNDORFF-NIELSEN [11, 12]) of the formalism is possible; then our integral defines the noninformative prior, i.e., the least informative ensemble. (The noninformative prior is typically improper, i.e., not a probability distribution, since  $\int 1$  is usually not defined).

While the Bayesian view gives, in my opinion, a misleading picture of statistical mechanics (see Appendix B), such an interpretation is formally allowed (cf. Appendix A) if – and only if – (i) *correct, complete and exact information about the expectation of all relevant quantities* is assumed to be known, and (ii) the noninformative prior is fixed by the above constructions, namely as the correctly weighted Liouville measure in classical physics and as the microcanonical ensemble in quantum physics. Only this guarantees that the ‘knowledge’ assumed and hence the results obtained are completely impersonal and objective. However, this kind of knowledge is clearly completely hypothetical and has nothing to do with the real, subjective knowledge of real observers. Thus, it is better to avoid any reference to knowledge; it is neither useful nor necessary but confuses the subject.

**Statistics.** In a context where many repeated experiments are feasible, states can be given a frequentist interpretation, where  $\langle g \rangle$  is the expectation of  $g$ , empirically defined as an average over many realizations. In this case,  $\text{Res}(g)$  becomes the standard deviation of  $g$ , divided by the absolute value of the expectation; therefore, it measures the relative accuracy of the realizations. However, as discussed in detail in the excellent survey by SKLAR [115], this interpretation has significant foundational problems, already in the framework of classical physics. And it seems especially inappropriate in equilibrium thermodynamics, where a tiny number of macroscopic observations on a single system completely determine its state to engineering accuracy.

In the following, we shall, therefore, completely avoid any reference to probability and statistics. While keeping the terminology of ensembles in the cases where it is established (the canonical and the grand canonical ensemble), we use the term ensemble<sup>6</sup> in a non-stochastic manner. We denote by it just a way of defining a state which provides for all quantities objective values satisfying the above properties. *In contrast to tradition, we take  $\langle \cdot \rangle$  not to have an intrinsic probabilistic meaning as an average over a large statistical ensemble of ‘true’ microstates.*

In this way, we delegate statistics to its role as *the art of interpreting measurements*, as in classical physics. Indeed, to have a consistent interpretation, real experiments must be designed such that they allow one to determine approximately the properties of the state under study, hence the values of all quantities of interest. The uncertainties in the experiments



imply approximations, which, if treated probabilistically, need an *additional* probabilistic layer accounting for measurement errors. Expectations from this secondary layer, which involve probabilistic statements about situations that are uncertain due to neglected but observable details (cf. PERES [100]), happen to have the same formal properties as the values on the primary layer (which contain a complete description of what is observable at a given energy scale), though their physical origin and meaning is completely different.

In the following, we only consider the primary level, where measurement errors are considered to be absent and an objective idealized description is assumed to be valid.

## 7 The zeroth law: Thermal states

We now restrict our attention to a restricted but very important class of Gibbs states, those describing thermal states.

In thermodynamics, one distinguishes between extensive and intensive variables. *Extensive variables* such as mass, charge, or volume depend additively on the size of the system; the global quantities are given by fields interpreted as densities integrated over the region occupied by the system. The conjugate *intensive variables* are given by fields interpreted as field strengths; they act as parameters defining the state. They cannot be viewed as densities; instead, their differences or gradients have physical significance as the sources for thermodynamic forces. In particular, in the single-phase global equilibrium case treated in Section 2, where the densities are constant, the extensive variables are densities multiplied by the system size, hence scale linearly with the size of the system, while intensive variables are invariant under a change of system size. (We do *not* use the alternative convention to call extensive any variable which scales linearly with the system size, and intensive any variable invariant under a change of system size.)

Thermal states are good models for macroscopic physical systems that are homogeneous on the level used for modeling. Indeed, as we shall see, they have all the properties traditionally postulated in thermodynamics. We distinguish four nested levels of thermal descriptions, *global*, *local*, *microlocal* and *quantum equilibrium*. The highest and computationally simplest level, global equilibrium, is concerned with macroscopic situations described by finitely many space- and time-independent variables. The next level, local equilibrium, treats macroscopic situations in a hydrodynamical or continuum mechanical description, where the relevant variables are finitely many space- and time-dependent fields, though for stirred chemical reactions, the space-dependence can be ignored. The next deeper level, microlocal<sup>8</sup> equilibrium, treats mesoscopic situations in a kinetic description, where the relevant variables are finitely many fields depending on time, position, and momentum; cf. BALIAN [8]. The bottom level is the microscopic regime, where we must consider quantum

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<sup>8</sup>The term microlocal for a phase space dependent analysis is taken from the literature on partial differential equations; see, e.g., MARTINEZ [84].

equilibrium, which is described in terms of quantum dynamical semigroups. The relations between the different description levels will be discussed in Section 13. Apart from descriptions on these clear-cut levels, there are also various hybrid descriptions, where the most important part of a system is described on a more detailed level than the remaining parts.

In global equilibrium, all thermal variables are constant 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 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 local or microlocal equilibrium, the same intuition applies, but with fields in place of variables. Then extensive variables are densities represented by distributions that can be meaningfully integrated over bounded regions, whereas intensive variables are nonsingular fields (e.g., pressure) whose integrals are physically irrelevant.

Although dynamics is important for systems not in global equilibrium, we ignore dynamical issues completely in the remainder of this paper. We take a strictly kinematic point of view, and look only at a single phase without chemical reactions. In a future paper, we shall extend the present setting to cover the dynamics of the nonequilibrium case and deduce quantitatively the dynamical laws (BERIS & ESWARDS [16], OETTINGER [97]) from microscopic properties, including phase formation, chemical reactions, and the approach to equilibrium; cf. BALIAN [8], GRABERT [50], RAU & MÜLLER [105], SPOHN [117].

In our present setting, the intensive variables are, as in Section 2, numbers characterizing certain Gibbs states, parameterizing the entropy. To each admissible combination of intensive variables there is a unique thermal state providing values for all quantities. The extensive variables then appear as the values of corresponding extensive quantities.

A basic extensive quantity present in each thermal system is the **Hamilton energy**  $H$ ; in addition, there are further basic extensive quantities which we call  $X_j$  ( $j \in J$ ) and collect in a vector  $X$ , indexed by  $J$ . The number and meaning of the extensive variables depends on the type of the system; typical examples are given in Table 1 in Section 13.

In the context of statistical mechanics (cf. Examples 4.1), the Euclidean \*-algebra  $\mathbb{E}$  is an algebra of functions (for classical physics) or linear operators (for quantum physics), and  $H$  is a particular function or linear operator called the **Hamiltonian**; specifying the precise form of the Hamiltonian is essentially equivalent to specifying the system under consideration. The form of the operators  $X_j$  depends on the level of thermal modeling; for further discussion, see Section 13.

For qualitative theory and for deriving semiempirical recipes, there is no need to know details about  $H$  or  $X_j$ ; it suffices to treat them as primitive objects. The advantage we gain from our less detailed setting is that a much simpler machinery than that of statistical

mechanics proper suffices to reconstruct all of *phenomenological* thermodynamics.

It is intuitively clear from the above informal definition of extensive variables that the only functions of independent extensive variables that are again extensive can be linear combinations, and it is a little surprising that *the whole machinery of equilibrium thermodynamics follows from a formal version of the simple assumption that in thermal states the entropy is extensive*. We take this to be the mathematical expression of the zeroth law and formalize this assumption in a precise mathematical definition.

For notational simplicity, we consider mainly the case of global equilibrium, where there are only finitely many extensive variables. Everything extends, however, with (formally trivial but from a rigorous mathematical view nontrivial) changes to local and microlocal equilibrium, where extensive variables are fields, provided the sums are replaced by appropriate integrals; cf. OETTINGER [97].

**7.1 Definition.** A **thermal system** is defined by a family of Hermitian **extensive variables**  $H$  and  $X_j$  ( $j \in J$ ) from a Euclidean  $*$ -algebra. A **thermal state** of a thermal system is a Gibbs state whose entropy  $S$  is a linear combination of the basic extensive quantities of the form

$$S = T^{-1} \left( H - \sum_{j \in J} \alpha_j X_j \right) = T^{-1} (H - \alpha \cdot X) \quad (\text{zeroth law of thermodynamics}) \quad (54)$$

with suitable real numbers  $T \neq 0$  and  $\alpha_j$  ( $j \in J$ ). (Here  $\alpha$  and  $X$  are the vectors with components  $\alpha_j$  ( $j \in J$ ) and  $X_j$  ( $j \in J$ , respectively.) Thus the value of an arbitrary quantity  $g$  is

$$\bar{g} := \langle g \rangle = \int e^{-\beta(H - \alpha \cdot X)} g, \quad (55)$$

where

$$\beta = \frac{1}{kT}. \quad (56)$$

The numbers  $\alpha_j$  are called the **intensive variables conjugate to**  $X_j$ , the number  $T$  is called the **temperature**, and  $\beta$  the **coldness**.  $\bar{S}, \bar{H}, \bar{X}, T$ , and  $\alpha$  are called the **thermal variables** of the system. Note that the extensive variables of traditional thermodynamics are in the present setting not represented by the extensive quantities  $S, H, X_j$  themselves but by their values  $\bar{S}, \bar{H}, \bar{X}$ .

Since we can write the zeroth law (54) in the form

$$H = TS + \alpha \cdot X, \quad (57)$$

called the **Euler equation**, the temperature  $T$  is considered to be the intensive variable conjugate to the entropy  $S$ .

As already indicated in Example 2.3, measuring intensive variables is based upon the empirical fact (which cannot be formulated precisely in our purely kinematic setting) that two

systems in close contact which allows free exchange of some extensive quantity tend to relax to a joint equilibrium state, in which the corresponding intensive variable is the same in both systems. If a small measuring device is brought into close contact with a large system, the joint equilibrium state will be only minimally different from the original state of the large system; hence the intensive variables of the measuring device will move to the values of the intensive variables of the large system in the location of the measuring device. This allows to read off their value from a calibrated scale.

Many treatises of equilibrium thermodynamics take this possibility of measuring temperature to be the contents of the zeroth law of thermodynamics. The present, different choice for the zeroth law is superior since it has a definite mathematical content which has far reaching consequences. Indeed, as we shall see, our definition already implies the first and second law, and (together with a quantization condition) the third law of thermodynamics.

**7.2 Remarks.** (i) We emphasize that the extensive quantities  $H$  and  $X_j$  are independent of the intensive quantities  $T$  and  $\alpha$ , while  $S$ , defined by (54), is an extensive quantity defined only when values for the intensive quantities are prescribed. Note that  $T$  and  $\alpha$  vary with the state, and the entropy depends on them via (54); hence values also depend on the particular state a system is in. It is crucial to distinguish between the quantities  $H$  or  $X_j$  (which are independent of  $T$  and  $\alpha$  and hence depend on the system but not on the state) and their values  $\overline{H} = \langle H \rangle$  or  $\overline{X}_j = \langle X_j \rangle$  (which change when the state of the system changes).

(ii) Although in thermodynamics, the emphasis is on the values of the thermal variables, it is important to realize that a thermal state gives complete information about the values (55) of *arbitrary* quantities, not only the extensive ones. The few numbers or fields specifying  $T$  and  $\alpha$  fully characterize a thermal state of a given system, while a general non-thermal state usually has a vastly higher complexity. In particular, global equilibrium is characterized by a small, finite number of variables, while already local equilibrium involves infinitely many degrees of freedom.

(iii) Of course, the number of parameters depends on the true physical situation. A system in local equilibrium only cannot be adequately described by the few variables characterizing global equilibrium. The question of selecting the right set of extensive quantities for an adequate description is discussed in Section 13.

(iv) An arbitrary linear combination

$$S = \gamma H + h_0 X_0 + \dots + h_s X_s \quad (58)$$

can be written in the form (54) with  $T = 1/\gamma$  and  $\alpha_j = -h_j/\gamma$ , provided that  $\gamma \neq 0$ ; and indeed, (58) is the mathematically more natural form, which also allows states of infinite temperature that are excluded in (54). However, the formulation as (54) seems to be unalterably fixed by tradition, so we shall use it here, too. This shows that the coldness  $\beta$  is a more natural variable than the temperature  $T$ ; it figures prominently in

statistical mechanics. In the limit  $T \rightarrow 0$ , a system becomes infinitely cold, giving intuition for the unattainability of zero absolute temperature. States of negative temperature, i.e., negative coldness, must therefore be considered to be hotter, i.e., less cold, than states of any positive temperature, cf. LANDAU & LIFSCHITZ [78]. To model thermal behavior at negative or infinite temperature, one can alternatively introduce a dummy temperature  $\widehat{T} = 1$ , a dummy Hamiltonian  $\widehat{H} = 0$ , and treating the true Hamiltonian and the coldness as additional components of  $X$  and  $\alpha$ , respectively.

(v) In mathematical statistics, there is a large body of work on *exponential families*, which is essentially the mathematical equivalent of the concept of a thermal state over a commutative algebra; see, e.g., BARNDORFF-NIELSEN [11]. In this context, the values of the extensive quantities define a *sufficient statistic*, from which the whole distribution can be reconstructed (cf. Theorem 8.4 below and the remarks on objective probability in Section 6). This is one of the reasons why exponential families provide a powerful machinery for statistical inference; see, e.g., BERNARDO & SMITH [17]. For recent extensions to quantum statistical inference, see, e.g., BARNDORFF-NIELSEN et al. [12] and the references there.

## 8 The equation of state

Not every combination  $(T, \alpha)$  of intensive variables defines a thermal state; the requirement that  $\langle 1 \rangle = 1$  enforces a restriction of  $(T, \alpha)$  to a manifold of admissible thermal states.

**8.1 Theorem.** *Suppose that  $T > 0$ .*

(i) *For any  $\kappa > 0$ , the **system function**  $\Delta$  defined by*

$$\Delta(T, \alpha) := \kappa T \log \int e^{-\beta(H - \alpha \cdot X)} \quad (59)$$

*is a convex function of  $T$  and  $\alpha$ . It vanishes only if  $T$  and  $\alpha$  are the intensive variables of a thermal state.*

(ii) *In a thermal state, the intensive variables are related by the **equation of state***

$$\Delta(T, \alpha) = 0. \quad (60)$$

*The **state space** is the set of  $(T, \alpha)$  satisfying (60).*

(iii) *The values of the extensive variables are given by*

$$\overline{S} = \Omega \frac{\partial \Delta}{\partial T}(T, \alpha), \quad \overline{X} = \Omega \frac{\partial \Delta}{\partial \alpha}(T, \alpha) \quad \text{for some } \Omega > 0, \quad (61)$$

*and the **phenomenological Euler equation***

$$\overline{H} = T \overline{S} + \alpha \cdot \overline{X}. \quad (62)$$

(iv) Regarding  $\bar{S}$  and  $\bar{X}$  as functions of  $T$  and  $\alpha$ , the matrix

$$\Sigma := \begin{pmatrix} \frac{\partial \bar{S}}{\partial T} & \frac{\partial \bar{S}}{\partial \alpha} \\ \frac{\partial \bar{X}}{\partial T} & \frac{\partial \bar{X}}{\partial \alpha} \end{pmatrix} \quad (63)$$

is symmetric and positive semidefinite; in particular, we have the **Maxwell reciprocity relations**

$$\frac{\partial \bar{X}_i}{\partial \alpha_j} = \frac{\partial \bar{X}_j}{\partial \alpha_i}, \quad \frac{\partial \bar{X}_i}{\partial T} = \frac{\partial \bar{S}}{\partial \alpha_i}, \quad (64)$$

and the **stability conditions**

$$\frac{\partial \bar{S}}{\partial T} \geq 0, \quad \frac{\partial \bar{X}_j}{\partial \alpha_j} \geq 0 \quad (j \in J). \quad (65)$$

*Proof.* By Theorem 5.2(i), the function  $\phi$  defined by

$$\phi(\alpha_0, \alpha) := \log \int e^{-(\alpha_0 H - \alpha \cdot X)} = -W(\alpha_0 H - \alpha \cdot X)$$

is a convex function of  $\alpha_0$  and  $\alpha$ . Put  $\Omega = \bar{k}/\kappa$ . Then, by Proposition C.4,

$$\Delta(T, \alpha) = -\kappa T W(\beta(H - \alpha \cdot X)) = \kappa T \phi\left(\frac{1}{\bar{k}T}, \frac{\alpha}{\bar{k}T}\right) \quad (66)$$

is also convex. The condition  $\Delta(T, \alpha) = 0$  is equivalent to

$$\int e^{-S/\bar{k}} = \int e^{-\beta(H - \alpha \cdot X)} = e^{\Delta/\kappa T} = 1,$$

the condition for a thermal state. This proves (i) and (ii).

(iii) The formulas for  $\bar{S}$  and  $\bar{X}$  follow by differentiation of (66) with respect to  $T$  and  $\alpha$ , using (44). Equation (62) follows by taking values in (57), noting that  $T$  and  $\alpha$  are real numbers.

(iv) By (iii), the matrix

$$\Sigma = \begin{pmatrix} \frac{\partial^2 \Delta}{\partial T^2} & \frac{\partial^2 \Delta}{\partial T \partial \alpha} \\ \frac{\partial^2 \Delta}{\partial \alpha \partial T} & \frac{\partial^2 \Delta}{\partial \alpha^2} \end{pmatrix}$$

is the Hessian matrix of the convex function  $\Delta$ . Hence  $\Sigma$  is symmetric and positive semidefinite. (64) expresses the symmetry of  $\Sigma$ , and (65) holds since the diagonal entries of a positive semidefinite matrix are nonnegative.  $\square$

**8.2 Remarks.** (i) For  $T < 0$ , the same results hold, with the change that  $\Delta$  is concave instead of convex,  $\Sigma$  is negative semidefinite, and the inequality signs in (65) are reversed. This is a rare situation; it can occur only in (nearly) massless systems embedded within (much heavier) matter, such as spin systems (cf. PURCELL & POUND [104]) or vortices in 2-dimensional fluids (cf. MONTGOMERY & JOYCE [87], EYINCK & SPOHN [42]). A massive thermal system couples significantly to kinetic energy. In this case, the total momentum  $p$  is an extensive quantity, related to the velocity  $v$ , the corresponding intensive variable, by  $p = Mv$ , where  $M$  is the extensive total mass of the system. From (61), we find that  $\bar{p} = \Omega \partial \Delta / \partial v$ , which implies that  $\Delta = \Delta|_{v=0} + \frac{\bar{M}}{2\Omega} v^2$ . Since the mass is positive, this expression is convex in  $v$ , not concave; hence  $T > 0$ . Thus, in a massive thermal system, the temperature must be positive.

(ii) In the application, the free scaling constant  $\kappa$  is usually chosen as  $\kappa = \bar{k}/\Omega$ , where  $\Omega$  is a measure of **system size**, e.g., the total volume or total mass of the system. In actual calculations from statistical mechanics, the integral is usually a function of the system size. To make the result independent of it, one performs the so-called thermodynamic limit  $\Omega \rightarrow \infty$ ; thus  $\Omega$  must be chosen in such a way that this limit is nontrivial. Extensivity in single phase global equilibrium then justifies treating  $\Omega$  as an arbitrary positive factor.

The equation of state shows that, apart from possible singularities describing so-called 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 phenomenological thermodynamics (cf. Section 2), one makes suitable, more or less heuristic assumptions on the form of the system function, while in **statistical mechanics**, one derives its form from (60) and specific choices for the quantities  $H$  and  $X$  within one of the settings described in Example 4.1. Given these choices, the main task is then the evaluation of the system function (59) since everything else can be computed from it. Frequently, (59) can be approximately evaluated from the cumulant expansion (42) and/or a mean field approximation (51).

An arbitrary Gibbs state is generally not a thermal state. However, we can try to approximate it by an equilibrium state.

**8.3 Theorem.** *Let  $\langle \cdot \rangle$  be a Gibbs state with entropy  $S$ . Then, for arbitrary  $(T, \alpha)$  satisfying  $T > 0$  and the equation of state (60), the values  $\bar{H} = \langle H \rangle$ ,  $\bar{S} = \langle S \rangle$ , and  $\bar{X} = \langle X \rangle$  satisfy*

$$\bar{H} \geq T\bar{S} - \alpha \cdot \bar{X}. \quad (67)$$

*Equality only holds if  $S$  is the entropy of a thermal state with intensive variables  $(T, \alpha)$ .*

*Proof.* The equation of state implies that  $S_c := T^{-1}(H - \alpha \cdot X)$  is the entropy of a thermal state. Now the assertion follows from Theorem 5.3, since  $\langle S \rangle \leq \langle S_c \rangle = T^{-1}(\langle H \rangle - \alpha \cdot \langle X \rangle)$ , with equality only if  $S = S_c$ .  $\square$

As the theorem shows, everything of macroscopic interest is deducible from an explicit formula for the system function. This explains why, in many situations, one can use thermodynamics very successfully as a phenomenological theory without having to bother about microscopic details. It suffices that a phenomenological expression for  $\Delta(T, \alpha)$  is available. In particular, the phenomenological axioms from Section 2 now follow by specializing the above to a **standard system**, characterized by the extensive quantities

$$H, X_0 = V, \quad X_j = N_j \quad (j \neq 0), \quad (68)$$

where, as before,  $V$  denotes the (positive) **volume** of the system, and each  $N_j$  denotes the (nonnegative) number of molecules of a fixed chemical composition (we shall call these **particles of species  $j$** ). However,  $H$  and the  $N_j$  are now quantities from  $\mathbb{E}$ , rather than thermal variables.

$$P := -\alpha_0 \quad (69)$$

is called **pressure**, and

$$\mu_j := \alpha_j \quad (j \neq 0) \quad (70)$$

the **chemical potential** of species  $j$ ; hence

$$\alpha \cdot X = -PV + \mu \cdot N.$$

Specializing the theorem, we find the phenomenological Euler equation

$$\bar{H} = T\bar{S} - PV + \mu \cdot \bar{N}. \quad (71)$$

For reversible changes, we have the first law of thermodynamics

$$d\bar{H} = Td\bar{S} - PdV + \mu \cdot d\bar{N} \quad (72)$$

and the Gibbs-Duhem equation

$$0 = \bar{S}dT - VdP + \bar{N} \cdot d\mu. \quad (73)$$

A comparison with Section 2 shows that dropping the bars from the values reproduces for  $T > 0$ ,  $P > 0$  and  $\bar{S} \geq 0$  the axioms of phenomenological thermodynamics, except for the extensivity outside equilibrium (which has local equilibrium as its justification). The assumption  $T > 0$  was justified in Remark 8.2(i), and  $\bar{S} \geq 0$  will be justified in Section 12. But I have been unable to find a theoretical argument which shows that the pressure of a standard system in the above sense must always be positive. (At  $T < 0$ , negative pressure is possible; see Example 8.5.) I'd appreciate getting information about this from my readers.

Apart from boundary effects, which become more and more unimportant as the system gets larger, the extensive quantities scale linearly with the volume. In the thermodynamic limit, corresponding to an idealized system infinitely extended in all directions, this becomes exact, although this can be proved rigorously only in simple situations, e.g., for hard sphere model systems (YANG & LEE [132]) or spin systems (GRIFFITHS [53]). A thorough



treatment of the thermodynamic limit (e.g., THIRRING [122], or, in the framework of large deviation theory, ELLIS [40]) in general needs considerably more algebraic and analytic machinery, e.g., the need to work in place of thermal states with more abstract KMS-states (which are limits of sequences of thermal states still satisfying a KMS condition (29)). Moreover, proving the existence of the limit requires detailed properties of the concrete microscopic description of the system.

For very small systems, typically atomic clusters or molecules,  $N$  is fixed and a **canonical ensemble** without the  $\mu \cdot N$  term is more appropriate. For the thermodynamics of small systems (see, e.g., (BUSTAMENTE et al. [25], GROSS [54], KRATKY [72]) such as a single cluster of atoms,  $V$  is still taken as a fixed reference volume, but now changes in the physical volume (adsorption or dissociation at the surface) are not represented in the system, hence need not respect the thermodynamic laws. For large surfaces (e.g., adsorption studies in chromatography [69, 85]), a thermal description is achievable by including additional variables (surface area and surface tension) to account for the boundary effects; but clearly, surface terms scale differently with system size than bulk terms.

Thus, whenever the thermal description is valid, computations can be done in a fixed reference volume  $V_0$  which we take as system size  $\Omega$ , and the true, variable volume  $V$  can always be represented in the Euclidean \*-algebra as a real number, so that in particular  $\bar{V} = V$ . Then (59) implies that, for the reference volume,

$$\Delta(T, \alpha) = \Omega^{-1} kT \log(e^{-\beta P \Omega} \int e^{-\beta(H-\mu \cdot N)}),$$

hence

$$\Delta(T, \alpha) = \Omega^{-1} kT (\log Z(T, \mu) - P \Omega) = P(T, \mu) - P, \quad (74)$$

where

$$Z(T, \mu) := \int e^{-\beta(H-\mu \cdot N)} \quad (75)$$

is the so-called **grand canonical partition function** of the system and

$$P(T, \mu) := \Omega^{-1} kT \log Z(T, \mu). \quad (76)$$

With our convention of considering a fixed reference volume and treating the true volume  $V$  as a scale factor (otherwise a thermodynamic limit would be needed), this expression is independent of  $V$ , since it relates intensive variables unaffected by scaling. The equation of state (60) therefore takes the form

$$P = P(T, \mu). \quad (77)$$

Quantitative expressions for the equation of state can often be computed from (75)–(76) using the cumulant expansion (42) and/or a mean field approximation (51). Note that these relations imply

$$e^{-\beta P(T, \mu) V} = \int e^{-\beta(H-\mu \cdot N)}.$$

Traditionally (see, e.g., GIBBS [48], HUANG [61], REICHL [106]), the thermal state corresponding to (74)–(76) is called a **grand canonical ensemble**, and the following results are taken as the basis for microscopic calculations from statistical mechanics.

**8.4 Theorem.** For a standard system in global equilibrium, values of an arbitrary quantity  $g$  can be calculated from (75) and

$$\langle g \rangle = Z(T, \mu)^{-1} \int e^{-\beta(H - \mu \cdot N)} g. \quad (78)$$

The values of the extensive quantities are given in terms of the equation of state (76) by

$$\bar{S} = V \frac{\partial P}{\partial T}(T, \mu), \quad \bar{N}_j = V \frac{\partial P}{\partial \mu_j}(T, \mu) \quad (79)$$

and the phenomenological Euler equation (71).

*Proof.* Equation (76) implies that

$$\begin{aligned} \langle g \rangle &= \int e^{-S/k} g = \int e^{-\beta(H + PV - \mu \cdot N)} g \\ &= e^{-\beta PV} \int e^{-\beta(H - \mu \cdot N)} g = Z(T, V, \mu)^{-1} \int e^{-\beta(H - \mu \cdot N)} g, \end{aligned}$$

giving (78). The formulas in (79) follow from (61) and (74).  $\square$

No thermodynamic limit was needed to derive the above results. Thus, everything holds – though with large limit resolutions in measurements – even for single small systems (BUSTAMANTE et al. [25], GROSS [54], KRATKY [72]).

**8.5 Example.** We consider the two level system from Example 4.4, using  $\Omega = 1$  as system size. From (75) and (76), we find  $Z(T, \mu) = 1 + e^{-E/kT}$ , hence

$$P(T, \mu) = kT \log(1 + e^{-E/kT}) = kT \log(e^{E/kT} + 1) - E.$$

From (78), we find

$$\bar{H} = \frac{E e^{-E/kT}}{1 + e^{-E/kT}} = \frac{E}{e^{E/kT} + 1}, \quad kT = \frac{E}{\log(E/\bar{H} - 1)}.$$

(This implies that a two-level system has negative temperature and negative pressure if  $\bar{H} > E/2$ .) The **heat capacity**  $C := d\bar{H}/dT$  takes the form

$$C = \frac{E^2}{kT^2} \frac{e^{E/kT}}{(e^{E/kT} + 1)^2}.$$

It exhibits a pronounced maximum, the so-called **Schottky bump** (cf. CALLEN [26]), from which  $E$  can be determined. In view of (109) below, this allows the experimental estimation of the spectral gap of a quantum system. The phenomenon persists to some extent for multilevel systems; see CIVITARESE et al. [32].

## 9 Description levels

So far, we have assumed a fixed selection of extensive quantities defining the thermal model. However, as indicated at the end of Section 2, observable differences from the conclusions derived from a thermal model imply that one or more conjugate pairs of thermal variables are missing in the model. In this section, we discuss in more detail the relation between different thermal models constructed on the basis of the same Euclidean \*-algebra by selecting different lists of extensive quantities.

Our first observation is the flexibility of the thermal setting. While the zeroth law may look very restrictive at first sight, by choosing a large enough family of extensive quantities the entropy of an *arbitrary* Gibbs state can be approximated arbitrarily well by a linear combination of these quantities.

The zeroth law thus simply appears as an embodiment of OCKHAM's razor<sup>9</sup> [96], freely paraphrased in modern form: that we should opt for the most economic model explaining a phenomenon – by restricting attention to the relevant extensive quantities only. At each time  $t$ , there is – except in degenerate cases – a *single* Gibbs state, with entropy  $S(t)$ , say, which best describes the system under consideration. Assuming the description by the Gibbs state as fundamental, its value is the objective, true value of the entropy, relative only to the algebra of quantities chosen to model the system. A description of the state in terms of a thermal system is therefore adequate if (and, under an observability qualification to be discussed below, only if), for all relevant times  $t$ , the entropy  $S(t)$  can be adequately approximated by a linear combination of the extensive quantities available at the chosen level of description.

The set of extensive variables depends on the application and on the desired accuracy of the model; it must be chosen in such a way that knowing the measured values of the extensive variables determines (to the accuracy specified) the complete behavior of the thermal system. Thus, the choice of extensive variables is (to the accuracy specified) completely determined by the level of accuracy with which the thermal description should fit the system's behavior. This forces everything else: The theory must describe the freedom available to characterize a particular thermal system with this set of extensive variables, and it must describe how the numerical values of interest can be computed for each state of each thermal system.

In contrast to the information theoretic approach where the choice of extensive quantities is considered to be the subjective matter of which observables an observer happens to have knowledge of, the only subjective aspect of our setting is the choice of the resolution of modeling. This fixes the amount of approximation tolerable in the ansatz, and hence the necessary list of extensive quantities. (Clearly, physics cannot be done without approximation, and the choice of a resolution is unavoidable. To remove even this trace of subjectivity,

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<sup>9</sup> frustra fit per plura quod potest fieri per pauciora

inherent in any approximation of anything, the entropy would have to be represented without any approximation, which would require to use as the algebra of quantities the still unknown theory of everything, and to demand that the extensive quantities exhaust this algebra.)

Table 1: Typical conjugate pairs of thermal variables and their contribution to the Euler equation. The signs are fixed by tradition. (in the gravitational term,  $m$  is the vector with components  $m_j$ , the mass of a particle of species  $j$ ,  $g$  the acceleration of gravity, and  $h$  the height.)

extensive $X_j$	intensive $\alpha_j$	contribution $\alpha_j X_j$
entropy $S$	temperature $T$	thermal, $TS$
particle number $N_j$	chemical potential $\mu_j$	chemical, $\mu_j N_j$
conformation tensor $C$	relaxation force $R$	conformational $\sum R_{jk} C^{jk}$
strain $\varepsilon^{jk}$	stress $\sigma_{jk}$	elastic, $\sum \sigma_{jk} \varepsilon^{jk}$
volume $V$	pressure $-P$	mechanical, $-PV$
surface $A_S$	surface tension $\gamma$	mechanical, $\gamma A_S$
length $L$	tension $J$	mechanical, $JL$
displacement $q$	force $-F$	mechanical, $-F \cdot q$
momentum $p$	velocity $v$	kinetic, $v \cdot p$
angular momentum $J$	angular velocity $\Omega$	rotational, $\Omega \cdot J$
charge $Q$	electric potential $\Phi$	electrical, $\Phi Q$
polarization $P$	electric field strength $E$	electrical, $E \cdot P$
magnetization $M$	magnetic field strength $B$	magnetical, $B \cdot M$
e/m field $F$	e/m field strength $-F^s$	electromagnetic, $-\sum F_{\mu\nu}^s F^{\mu\nu}$
mass $M = m \cdot N$	gravitational potential $gh$	gravitational, $ghM$
energy-momentum $U$	metric $g$	gravitational, $\sum g_{\mu\nu} U^{\mu\nu}$

In general, which quantities need to be considered depends on the resolution with which the system is to be modeled – the higher the resolution the larger the family of extensive quantities. Thus – whether we describe bulk matter, surface effects, impurities, fatigue, decay, chemical reactions, or transition states, – the thermal setting remains the same since it is a universal approximation scheme, while the number of degrees of freedom increases with increasingly detailed models.

In phenomenological thermodynamics, the relevant extensive quantities are precisely those variables that are observed to make a difference in modeling the phenomenon of interest. Table 1 gives typical extensive variables, their intensive conjugate variables, and their

contribution to the Euler equation<sup>10</sup>. Some of the extensive variables and their intensive conjugates are vectors or (in elasticity theory, the theory of complex fluids, and in the relativistic case) tensors; cf. BALIAN [7] for the electromagnetic field and BERIS & EDWARDS [16], ÖTTINGER [97] for complex fluids.

To analyze the relation between two different thermal description levels, we compare a coarse system and a more detailed system quantitatively, taking for simplicity the temperature constant, so that the  $T$ -dependence can be suppressed in the formulas, and states are completely determined by  $\alpha$ .

The fine system will be written as before, the variables and quantities associated with the coarser system get an additional index  $c$ . In order to be able to compare the two systems, we assume that one is a refinement of the other, so that the extensive quantities of the coarse system are  $X_c = CX$ , with a fixed matrix  $C$  with linearly independent rows, whose components tell how the components of  $X_c$  are built from those of  $X$ . The entropy of the coarse system is then given by

$$S_c = T^{-1}(H - \alpha_c \cdot X_c) = T^{-1}(H - \alpha_c \cdot CX) = T^{-1}(H - \alpha^* \cdot X),$$

where

$$\alpha^* = C^T \alpha_c. \quad (80)$$

Thus, the thermal states of the coarse model are simply the states of the detailed model for which the intensive parameter vector  $\alpha$  is of the form  $\alpha = C^T \alpha_c$  for some  $\alpha_c$ . Thus the coarse state space can simply be viewed as a lower-dimensional subspace of the detailed state space. Therefore one expects the coarse description to be adequate precisely when the detailed state is close to the coarse state space, with an accuracy determined by the desired fidelity of the coarse model. Since the relative entropy (50),

$$\langle S_c - S \rangle = \langle T^{-1}(H - \alpha_c \cdot CX) - T^{-1}(H - \alpha \cdot X) \rangle = \langle T^{-1}(\alpha - C^* \alpha_c) \cdot X \rangle, \quad (81)$$

measures the amount of information in the detailed state which cannot be explained by the coarse state, it is sensible to associate to an arbitrary detailed state  $\alpha$  the coarse state  $\alpha_c$  determine by minimizing (81). If  $\alpha^* = C^T \alpha_c \approx \alpha$  then

$$S_c = T^{-1}(H - \alpha^* \cdot X) \approx T^{-1}(H - \alpha \cdot X) = S,$$

---

<sup>10</sup> The Euler equation, which contains the energy contributions specified in the table, looks like an energy balance. But since  $S$  is undefined, this formal balance has no contents apart from defining the entropy  $S$  in terms of the energy and other contributions. The energy balance is rather given by the first law discussed later, and is about *changes* in energy. Conservative work contributions are exact differentials. For example, the mechanical force  $F = -dV(q)/dq$  translates into the term  $-F \cdot dq = dV(q)$  of the first law, corresponding to the term  $-F \cdot q$  in the Euler equation. The change of the kinetic energy  $E_{\text{kin}} = mv^2/2$  contribution of linear motion with velocity  $v$  and momentum  $p = mv$  is  $dE_{\text{kin}} = d(mv^2/2) = mv \cdot dv = v \cdot dp$ , which is exactly what one gets from the  $v \cdot p$  contribution in the Euler equation. Since  $v \cdot p = mv^2$  is larger than the kinetic energy, this shows that motion implies a contribution to the entropy of  $(E_{\text{kin}} - v \cdot p)/T = -mv^2/2T$ . A similar argument applies to the angular motion of a rigid body in its rest frame, providing the term involving angular velocity and angular momentum.

and the coarse description is adequate. If  $\alpha^* \not\approx \alpha$ , there is no a priori reason to trust the coarse model, and we have to investigate to which extent its predictions will significantly differ from those of the detailed model. One expects the differences to be significant; however, in practice, there are difficulties if there are limits on our ability to prepare particular detailed states. The reason is that the entropy and chemical potentials can be prepared and measured only by comparison with states of sufficiently known states. A first sign of this is the gauge freedom in ideal gases discussed in Example 2.3, which implies that different models of the same situation may have nontrivial differences in Hamilton energy, entropy, and chemical potential. This ambiguity persists in more perplexing situations:

### 9.1 Example. (The Gibbs paradox)

Suppose that we have an ideal gas of two species  $j = 1, 2$  of particles which are experimentally indistinguishable. Suppose that in the samples available for experiments, the two species are mixed in significantly varying proportions  $N_1 : N_2 = q_1 : q_2$  which, by assumption, have no effect on the observable properties; in particular, their values are unknown but varying. The detailed model treats them as distinct, the coarse model as identical. Reverting to the barless notation of Section 2, we have

$$X = \begin{pmatrix} V \\ N_1 \\ N_2 \end{pmatrix}, \quad \alpha = \begin{pmatrix} -P \\ \mu_1 \\ \mu_2 \end{pmatrix},$$

and, assuming  $C = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c_1 & c_2 \end{pmatrix}$  for suitable  $c_1, c_2 > 0$ ,

$$X_c = \begin{pmatrix} V \\ N_c \end{pmatrix} = \begin{pmatrix} V \\ c_1 N_1 + c_2 N_2 \end{pmatrix}, \quad \alpha_c = \begin{pmatrix} -P \\ \mu_c \end{pmatrix}.$$

From the known proportions, we find

$$N_j = x_j N_c, \quad x_j = \frac{q_j}{c_1 q_1 + c_2 q_2}.$$

The mixture behaves like an ideal gas of a single species, hence

$$PV = kTN_c, \quad H = h_c(T)N_c, \quad \mu_c = kT \log \frac{kTN_c}{V\pi_c}.$$

Now  $N_c = (kT)^{-1}PV = \sum N_j = \sum x_j N_c$  implies that  $x_1 + x_2 = 1$ . Because of indistinguishability, this must hold for any choice of  $q_1, q_2 \geq 0$ ; for the two choices  $q_1 = 0$  and  $q_2 = 0$ , we get  $c_1 = c_2 = 1$ , hence  $N_c = \sum N_j$ , and the  $x_j$  are mole fractions. Similarly, if we use for all species  $j$  the same normalization for fixing the gauge freedom, the relation  $h_c(T)N_c = H = \sum h_j(T)N_j = \sum h_j(T)x_j N_c$  implies for varying mole fractions that  $h_j(T) = h_c(T)$  for  $j = 1, 2$ . From this, we get  $\pi_j(T) = \pi_c(T)$  for  $j = 1, 2$ . Thus

$$H - H_c = \sum h_j(T)N_j - h_c(T)N_c = 0,$$

$$\mu_j - \mu_c = kT \log \frac{kTN_j}{V\pi_j} - kT \log \frac{kTN_c}{V\pi_c} = kT \log x_j,$$

the Gibbs energy satisfies

$$G - G_c = \sum \mu_j N_j - \mu_c N_c = \sum (\mu_j - \mu_c) N_j = kTN_c \sum x_j \log x_j,$$

and the entropy satisfies

$$\begin{aligned} S - S_c &= T^{-1}(H - PV + G) - T^{-1}(H_c - PV + G_c) \\ &= T^{-1}(G - G_c) = kN_c \sum x_j \log x_j. \end{aligned}$$

This term is called the **entropy of mixing**. Its occurrence is referred to as Gibbs paradox (cf. JAYNES [65], TSENG & CATICHA [125], ALLAHVERDYAN & NIEUWENHUIZEN [4], UFFINK [126, Section 5.2]). It seems to say that there are two different entropies, depending on how we choose to model the situation. For fixed mole fractions, the paradox can be resolved upon noticing that the fine and the coarse description differ only by a choice of gauge; the gauge is unobservable anyway, and the entropy is determined only when the gauge is fixed.

However, if the mole fractions vary, the fine and the coarse description differ significantly. If the detailed model is correct, the coarse model gives a wrong description for the entropy and the chemical potentials. However, this difference is observable only if we know processes which affect the different species differently, such as a difference in mass, which allows a mechanical separation, in molecular size or shape, which allows their separation by a semipermeable membrane, in spin, which allows a magnetic separation, or in scattering properties of the particles, which may allow a chemical or radiation-based differentiation. In each of these cases, the particles become distinguishable, and the coarse description becomes inadequate.

If we cannot separate the species to some extent, we cannot prepare equilibrium ensembles at fixed mole fraction. But this would be necessary to calibrate the chemical potentials, since fixed chemical potentials can be prepared only through chemical contact with substances with known chemical potentials, and the latter must be computed from mole fractions.

Generalizing from the example, we conclude that even when both a coarse model and a more detailed model are faithful to all experimental information possible at a given description level, there is no guarantee that they agree in the values of all thermal variables of the coarse model. In the language of control theory (see, e.g., LJUNG [82]), agreement is guaranteed only when all parameters of the more detailed models are observable.

On the other hand, all observable state functions of the detailed system which depend only on the coarse state must and will have the same value within the experimental accuracy if both models are adequate descriptions of the situation. Thus, while the values of some variables need not be experimentally determinable, the validity of a model is an objective

property. Therefore, preferences for one or the other of two valid models can only be based on other criteria. The criterion usually employed in this case is Ockham's razor<sup>9</sup>, although there may be differences of opinion on what counts as the most economic model. In particular, a fundamental description of macroscopic matter by means of quantum mechanics is hopelessly overspecified in terms of the number of degrees of freedom needed for comparison with experiment, most of which are in principle unobservable by equipment made of ordinary matter. But it is often the most economical model in terms of description length (though extracting the relevant information from it may be difficult). Thus, different people may well make different rational choices, or employ several models simultaneously.

The objectivity of a model description implies that, as soon as a discrepancy with experiment is reliably found, the model must be replaced by a more detailed (or altogether different) model. This is indeed what happened with the textbook example of the Gibbs paradox situation, ortho and para hydrogen, cf. BONHOEFFER & HARTECK [20], FARKAS [43]. Hydrogen seemed at first to be a single substance, but then thermodynamic data forced a refined description.

Similarly, in spin echo experiments (see, e.g., HAHN [55, 56], ROTHSTEIN [114], RIDDERBOS & REDHEAD [109]), the specially prepared system appears to be in equilibrium but, according to Callen's empirical definition<sup>5</sup> it is not – the surprising future behavior (for someone not knowing the special preparation) shows that some correlation variables were neglected that are needed for a correct description. Indeed, everywhere in science, we strive for explaining surprising behavior by looking for the missing variables needed to describe the system correctly!

GRAD [51] expresses this as "the adoption of a new entropy is forced by the discovery of new information". More precisely, the adoption of a new *model* is forced, since the old model is simply wrong under the new conditions and remains valid only under some restrictions. Thus this is not a property of entropy alone, but of all concepts in models of reality relating to effects not observable (in the sense of control theory discussed above).

Observability issues aside, the coarser description usually has a more limited range of applicability; with the qualification discussed in the example, it is generally restricted to those systems whose detailed intensive variable vector  $\alpha$  is close to the subspace of vectors of the form  $C^T\alpha$  reproducible in the coarse model. Finding the right family of thermal variables is therefore a matter of discovery, not of subjective choice. This is further discussed in Section 13.

## 10 The first law: Energy balance

We now discuss relations between changes of the values of extensive or intensive variables, as expressed by the first law of thermodynamics. To derive the first law in full generality,



we use the concept of reversible transformations introduced in Section 2. Corresponding to such a transformation, there is a family of thermal states  $\langle \cdot \rangle_\lambda$  defined by

$$\langle f \rangle_\lambda = \int e^{-\beta(\lambda)(H - \alpha(\lambda) \cdot X)} f, \quad \beta(\lambda) = \frac{1}{\bar{k}T(\lambda)}.$$

**Important:** In case of local or microlocal equilibrium, where the thermal system carries a dynamics, it is important to note that reversible transformations are fictitious transformations which have nothing to do with how the system changes with time, or whether a process is reversible in the dynamical sense that both the process and the reverse process can be realized dynamically. The time shift is generally *not* a reversible transformation.

We use differentials corresponding to reversible transformations; writing  $f = S/\bar{k}$ , we can delete the index  $f$  from the formulas in Section 4. In particular, we write the Kubo inner product (32) as

$$\langle g; h \rangle := \langle g; h \rangle_{S/\bar{k}}. \quad (82)$$

**10.1 Proposition.** *The value  $\bar{g}(T, \alpha) := \langle g(T, \alpha) \rangle$  of every (possibly  $T$ - and  $\alpha$ -dependent) quantity  $g(T, \alpha)$  is a state variable satisfying the **differentiation formula***

$$d\langle g \rangle = \langle dg \rangle - \langle g - \bar{g}; dS \rangle / \bar{k}. \quad (83)$$

*Proof.* That  $\bar{g}$  is a state variable is an immediate consequence of the zeroth law (54) since the entropy depends on  $T$  and  $\alpha$  only. The differentiation formula follows from (43) and (82).  $\square$

**10.2 Theorem.** *For reversible changes, we have the **first law of thermodynamics***

$$d\bar{H} = Td\bar{S} + \alpha \cdot d\bar{X} \quad (84)$$

and the **Gibbs-Duhem equation**

$$0 = \bar{S}dT + \bar{X} \cdot d\alpha. \quad (85)$$

*Proof.* Differentiating the equation of state (60), using the chain rule (10), and simplifying using (61) gives the Gibbs-Duhem equation (85). If we differentiate the phenomenological Euler equation (62), we obtain

$$d\bar{H} = Td\bar{S} + \bar{S}dT + \alpha \cdot d\bar{X} + \bar{X} \cdot d\alpha,$$

and using (85), this simplifies to the first law of thermodynamics.  $\square$

Because of the form of the energy terms in the first law (84), one often uses the analogy to mechanics and calls the intensive variables **generalized forces**, and differentials of extensive variables **generalized displacements**.

For the Gibbs-Duhem equation, we give a second proof which provides additional insight. Since  $H$  and  $X$  are fixed quantities for a given system, they do not change under reversible transformations; therefore

$$dH = 0, \quad dX = 0.$$

Differentiating the Euler equation (57), therefore gives the relation

$$0 = TdS + SdT + X \cdot d\alpha. \quad (86)$$

On the other hand,  $S$  depends explicitly on  $T$  and  $\alpha$ , and by Corollary C.3,

$$\langle dS \rangle = \int e^{-S/k} dS = kd \left( \int e^{-S/k} \right) = kd1 = 0, \quad (87)$$

taking values in (86) implies again the Gibbs-Duhem equation. Equation (86) can also be used to get information about limit resolutions.

### 10.3 Theorem.

(i) Let  $g$  be a quantity depending continuously differentiable on the intensive variables  $T$  and  $\alpha$ . Then

$$\langle g - \bar{g}; S - \bar{S} \rangle = kT \left( \frac{\partial \bar{g}}{\partial T} - \left\langle \frac{\partial g}{\partial T} \right\rangle \right), \quad (88)$$

$$\langle g - \bar{g}; X_j - \bar{X}_j \rangle = kT \left( \frac{\partial \bar{g}}{\partial \alpha_j} - \left\langle \frac{\partial g}{\partial \alpha_j} \right\rangle \right), \quad (89)$$

(ii) If the extensive variables  $H$  and  $X_j$  ( $j \in J$ ) are pairwise commuting then

$$\langle (S - \bar{S})^2 \rangle = kT \frac{\partial \bar{S}}{\partial T}, \quad (90)$$

$$\langle (X_j - \bar{X}_j)(S - \bar{S}) \rangle = kT \frac{\partial \bar{X}_j}{\partial T} \quad (j \in J), \quad (91)$$

$$\langle (X_j - \bar{X}_j)(X_k - \bar{X}_k) \rangle = kT \frac{\partial \bar{X}_j}{\partial \alpha_k} \quad (j, k \in J), \quad (92)$$

$$\text{Res}(S) = \sqrt{\frac{kT}{\bar{S}^2} \frac{\partial \bar{S}}{\partial T}}, \quad \text{Res}(X_j) = \sqrt{\frac{kT}{\bar{X}_j^2} \frac{\partial \bar{X}_j}{\partial \alpha_j}}, \quad (93)$$

$$\text{Res}(H) = \sqrt{\frac{kT}{\bar{H}^2} \left( T \frac{\partial \bar{H}}{\partial T} + \alpha \cdot \frac{\partial \bar{H}}{\partial \alpha} \right)}. \quad (94)$$

*Proof.* Multiplying the differentiation formula (83) by  $kT$  and using (86), we find, for arbitrary reversible transformations,

$$kT(d\langle g \rangle - \langle dg \rangle) = \langle g - \bar{g}; S \rangle dT + \langle g - \bar{g}; X \rangle \cdot d\alpha.$$

Dividing by  $d\lambda$  and choosing  $\lambda = T$  and  $\lambda = \alpha_j$ , respectively, gives

$$\langle g - \bar{g}; S \rangle = kT \left( \frac{\partial \bar{g}}{\partial T} - \left\langle \frac{\partial g}{\partial T} \right\rangle \right), \quad \langle g - \bar{g}; X_j \rangle = kT \left( \frac{\partial \bar{g}}{\partial \alpha_j} - \left\langle \frac{\partial g}{\partial \alpha_j} \right\rangle \right).$$

(i) follows upon noting that  $\langle g - \bar{g}; h - \bar{h} \rangle = \langle g - \bar{g}; h \rangle$  since by (35),

$$\langle g - \bar{g}; \bar{h} \rangle = \langle g - \bar{g} \rangle \bar{h} = (\langle g \rangle - \bar{g}) \bar{h} = 0.$$

If the extensive variables  $H$  and  $X_j$  ( $j \in J$ ) are pairwise commuting then we can use (36) to eliminate the Kubo inner product, and by choosing  $g$  as  $S$  and  $X_j$ , respectively, we find (90)–(92). The limit resolutions (93) now follow from (53) and the observation that  $\langle (g - \bar{g})^2 \rangle = \langle (g - \bar{g})g \rangle - \langle g - \bar{g} \rangle \bar{g} = \langle (g - \bar{g})g \rangle = \langle g^2 \rangle - \bar{g}^2$ . The limit resolution (94) follows similarly from

$$\begin{aligned} \text{Res}(H)^2 &= \langle H - \bar{H}; H - \bar{H} \rangle = T \langle H - \bar{H}; S - \bar{S} \rangle + \alpha \cdot \langle H - \bar{H}; X - \bar{X} \rangle \\ &= kT \left( T \frac{\partial \bar{H}}{\partial T} + \alpha \cdot \frac{\partial \bar{H}}{\partial \alpha_j} \right). \end{aligned}$$

□

Note that higher order central moments can be obtained in the same way, substituting more complicated expressions for  $f$  and using the formulas for the lower order moments to evaluate the right hand side of (88) and (89).

The extensive variables scale linearly with the system size  $\Omega$  of the system. Hence, the limit resolution of the extensive quantities is  $O(\sqrt{k/\Omega})$  in regions of the state space where the extensive variables depend smoothly on the intensive variables. Since  $k$  is very small, they are negligible unless the system considered is very tiny. Thus, macroscopic thermal variables can generally be obtained with fairly high precision. An exception is close to critical points where the extensive variables are not differentiable, and their derivatives can therefore become huge. In particular, in the thermodynamic limit  $\Omega \rightarrow \infty$ , uncertainties are absent except close to a critical point, where they lead to critical opacity.

**10.4 Corollary.** *For a standard thermal system,*

$$\text{Res}(S) = \sqrt{\frac{kT}{\bar{S}^2} \frac{\partial \bar{S}}{\partial T}}, \quad \text{Res}(N_j) = \sqrt{\frac{kT}{\bar{N}_j^2} \frac{\partial \bar{N}_j}{\partial \mu_j}}, \quad (95)$$

$$\text{Res}(H) = \sqrt{\frac{kT}{\bar{H}^2} \left( T \frac{\partial \bar{H}}{\partial T} + P \frac{\partial \bar{H}}{\partial P} + \mu \cdot \frac{\partial \bar{H}}{\partial \mu} \right)}. \quad (96)$$

*Proof.* Use (90) and (92). □

Note that  $\text{Res}(V) = 0$  since we regarded  $V$  as a number.

# 11 The second law: Extremal principles

The extremal principles of the second law of thermodynamics assert that in a nonthermal state, some energy expression depending on one of a number of standard boundary conditions is strictly larger than that of related thermal states. The associated thermodynamic potentials can be used in place of the system function to calculate all thermal variables given half of them. Thus, like the system function, thermodynamic potentials give a complete summary of the equilibrium properties of homogeneous materials. We only discuss the **Hamilton potential**

$$U(\bar{S}, \bar{X}) := \max_{T, \alpha} \{T\bar{S} + \alpha \cdot \bar{X} \mid \Delta(T, \alpha) = 0, T > 0\}$$

and the **Helmholtz potential**

$$A(T, \bar{X}) := \max_{\alpha} \{\alpha \cdot \bar{X} \mid \Delta(T, \alpha) = 0\};$$

other potentials can be handled in a similar way.

## 11.1 Theorem. (Second law of thermodynamics)

(i) In an arbitrary state,

$$\bar{H} \geq U(\bar{S}, \bar{X}),$$

with equality iff the state is a thermal state of positive temperature. The remaining thermal variables are then given by

$$T = \frac{\partial U}{\partial \bar{S}}(\bar{S}, \bar{X}), \quad \alpha = \frac{\partial U}{\partial \bar{X}}(\bar{S}, \bar{X}), \quad (97)$$

$$U = \bar{H} = U(\bar{S}, \bar{X}). \quad (98)$$

In particular, a thermal state of positive temperature is uniquely determined by the values of  $\bar{S}$  and  $\bar{X}$ .

(ii) Let  $T > 0$ . Then, in an arbitrary state,

$$\bar{H} - T\bar{S} \geq A(T, \bar{X}),$$

with equality iff the state is a thermal state of temperature  $T$ . The remaining thermal variables are then given by

$$\bar{S} = -\frac{\partial A}{\partial T}(T, \bar{X}), \quad \alpha = \frac{\partial A}{\partial \bar{X}}(T, \bar{X}), \quad (99)$$

$$\bar{H} = T\bar{S} + \alpha \cdot \bar{X} = A(T, \bar{X}) + T\bar{S}. \quad (100)$$

In particular, a thermal state of positive temperature is uniquely determined by the values of  $T$  and  $\bar{X}$ .

*Proof.* This is proved in the same way as Theorem 3.2; thus we give no details.  $\square$

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

**11.2 Theorem.**

(i) The function  $U(\bar{S}, \bar{X})$  is a convex function of its arguments which is positive homogeneous of degree 1, i.e., for real  $\lambda, \lambda^1, \lambda^2 \geq 0$ ,

$$U(\lambda\bar{S}, \lambda\bar{X}) = \lambda U(\bar{S}, \bar{X}), \quad (101)$$

$$U(\lambda^1\bar{S}^1 + \lambda^2\bar{S}^2, \lambda^1\bar{X}^1 + \lambda^2\bar{X}^2) \leq \lambda^1 U(\bar{S}^1, \bar{X}^1) + \lambda^2 U(\bar{S}^2, \bar{X}^2). \quad (102)$$

(ii) The function  $A(T, \bar{X})$  is a convex function of  $X$  which is positive homogeneous of degree 1, i.e., for real  $\lambda, \lambda^1, \lambda^2 \geq 0$ ,

$$A(T, \lambda\bar{X}) = \lambda A(T, \bar{X}), \quad (103)$$

$$A(T, \lambda^1\bar{X}^1 + \lambda^2\bar{X}^2) \leq \lambda^1 A(T, \bar{X}^1) + \lambda^2 A(T, \bar{X}^2). \quad (104)$$

*Proof.* This is proved in the same way as Theorem 3.3; thus we give no details.  $\square$

The extremal principles imply energy dissipation properties for time-dependent states. Since the present kinematical setting does not have a proper dynamical framework, it is only possible to outline the implications without going much into details.

**11.3 Theorem.**

(i) For any time-dependent system for which  $S$  and  $X$  remain constant and which converges to a thermal state with positive temperature, the Hamilton energy  $\langle H \rangle$  attains its global minimum in the limit  $t \rightarrow \infty$ .

(ii) For any time-dependent system maintained at fixed temperature  $T > 0$ , for which  $X$  remains constant and which converges to a thermal state, the Helmholtz energy  $\langle H - TS \rangle$  attains its global minimum in the limit  $t \rightarrow \infty$ .

*Proof.* This follows directly from Theorem 11.1.  $\square$

This result is the shadow of a more general, dynamical observation (that, of course, cannot be proved from kinematic assumptions alone but would require a dynamical theory). Indeed, it is a universally valid empirical fact that in all natural time-dependent processes, energy is lost or dissipated, i.e., becomes macroscopically unavailable, unless compensated by energy provided by the environment. Details go beyond the present framework, which adopts a strictly kinematic setting.

## 12 The third law: Quantization

The third law of thermodynamics asserts that the value of the entropy is always nonnegative. But it cannot be deduced from our axioms without making a further assumption, as a simple example demonstrates.

**12.1 Example.** The algebra  $\mathbb{E} = \mathbb{C}^m$  with pointwise operations is a Euclidean  $*$ -algebra for any integral of the form

$$\int f = \frac{1}{N} \sum_{n=1}^N w_n f_n \quad (w_n > 0);$$

the axioms are trivial to verify. For this integral the state defined by

$$\langle f \rangle = \frac{1}{N} \sum_{n=1}^N f_n,$$

is a state with entropy  $S$  given by  $S_n = k \log w_n$ . The value of the entropy

$$\bar{S} = \frac{1}{N} \sum_{n=1}^m S_n = \frac{k}{N} \log \prod_{n=1}^N w_n,$$

is negative if we choose the  $w_n$  such that  $\prod w_n < 1$ .

Thus, we need an additional condition which guarantees the validity of the third law. Since the third law is also violated in classical statistical mechanics, which is a particular case of the present setting, we need a condition which forbids the classical interpretation of our axioms.

We take our inspiration from a simple information theoretic model of states discussed in Appendix A, which has this property. (Indeed, the third law is a necessary requirement for the interpretation of the value of the entropy as a measure of internal complexity, as discussed there.) There, the integral is a sum over the components, and, since functions were defined componentwise,

$$\int F(f) = \sum_{n \in \mathcal{N}} F(f_n). \quad (105)$$

We say that a quantity  $f$  is **quantized** iff (105) holds with a suitable **spectrum**  $\{f_n \mid n \in \mathcal{N}\}$  for all functions  $F$  for which  $F(f)$  is strongly integrable; in this case, the  $f_n$  are called the **levels** of  $f$ . For example, in the quantum setting all trace class linear operators are quantized quantities, since these always has a discrete spectrum.

Quantization is the additional ingredient needed to derive the third law:

**12.2 Theorem. (Third law of thermodynamics)**

If the entropy  $S$  is quantized then  $\bar{S} \geq 0$ . Equality holds iff the entropy has a single level only ( $|\mathcal{N}| = 1$ ).

*Proof.* We have

$$1 = \int \rho = \int e^{-S/k} = \sum_{n \in \mathcal{N}} e^{-S_n/k} = \sum_{n \in \mathcal{N}} \rho_n, \quad (106)$$

where all  $\rho_n = e^{-S_n/k} > 0$ , and

$$\bar{S} = \int S \rho = \int S e^{-S/k} = \sum_{n \in \mathcal{N}} S_n e^{-S_n/k} = \sum_{n \in \mathcal{N}} S_n \rho_n. \quad (107)$$

If  $\mathcal{N} = \{n\}$  then (106) implies  $\rho_n = 1$ ,  $S_n = 0$ , and (107) gives  $\bar{S} = 0$ . And if  $|\mathcal{N}| > 1$  then (106) gives  $\rho_n < 1$ , hence  $S_n > 0$  for all  $n \in \mathcal{N}$ , and (107) implies  $\bar{S} > 0$ .  $\square$

In quantum chemistry, energy  $H$ , volume  $V$ , and particle numbers  $N_1, \dots, N_s$  form a quantized family of pairwise commuting Hermitian variables. Indeed, the Hamiltonian  $H$  has discrete energy levels if the system is confined to a finite volume,  $V$  is a number, hence has a single level only, and  $N_j$  counts particles hence has as levels the nonnegative integers. As a consequence, the entropy  $S = T^{-1}(H + PV - \mu \cdot N)$  is quantized, too, so that the third law of thermodynamics is valid. The number of levels is infinite, so that the value of the entropy is positive.

A zero value of the entropy (**absolute zero**) is therefore an idealization which cannot be realized in practice. But Theorem 12.2 implies in this idealized situation that entropy and hence the joint spectrum of  $(H, V, N_1, \dots, N_s)$  can have a single level only.

This is the situation discussed in ordinary quantum mechanics (pure energy states at fixed particle numbers). It is usually associated with the limit  $T \rightarrow 0$ , though at absolute temperature  $T = 0$ , i.e., infinite coldness  $\beta$ , the thermal formalism fails (but low  $T$  asymptotic expansions are possible).

To see the behavior close to this limit, we consider for simplicity a canonical ensemble with Hamiltonian  $H$  (Example 4.4); thus the particle number is fixed. Since  $S$  is quantized, the spectrum of  $H$  is discrete, so that there is a finite or infinite sequence  $E_0 < E_1 < E_2 < \dots$  of distinct energy levels. Denoting by  $P_n$  the (rank  $d_n$ ) orthogonal projector to the  $d_n$ -dimensional eigenspace with energy  $E_n$ , we have the spectral decomposition

$$\phi(H) = \sum_{n \geq 0} \phi(E_n) P_n$$

for arbitrary functions  $\phi$  defined on the spectrum. In particular,

$$e^{-\beta H} = \sum e^{-\beta E_n} P_n.$$

The partition function is

$$Z = \text{tr} e^{-\beta H} = \sum e^{-\beta E_n} \text{tr} P_n = \sum e^{-\beta E_n} d_n.$$

As a consequence,

$$e^{-S/k} = Z^{-1} e^{-\beta H} = \frac{\sum e^{-\beta E_n} P_n}{\sum e^{-\beta E_n} d_n} = \frac{\sum e^{-\beta(E_n - E_0)} P_n}{\sum e^{-\beta(E_n - E_0)} d_n},$$

hence values take the form

$$\langle f \rangle = \int e^{-S/k} f = \int \left( \frac{\sum e^{-\beta(E_n - E_0)} P_n}{\sum e^{-\beta(E_n - E_0)} d_n} \right). \quad (108)$$

From this representation, we see that only the energy levels  $E_n$  with

$$E_n \leq E_0 + O(kT)$$

contribute to a canonical ensemble of temperature  $T$ . If the temperature  $T$  is small enough, so that  $kT \ll E_2 - E_0$ , the exponentials  $e^{-\beta(E_n - E_0)}$  with  $n \geq 2$  can be neglected, and we find

$$e^{-S/k} \approx \frac{P_0 + e^{-\beta(E_1 - E_0)} P_1}{d_0 + e^{-\beta(E_1 - E_0)} d_1} = \frac{P_0}{d_0} + \frac{d_0 P_1 - d_1 P_0}{d_0(e^{\beta(E_1 - E_0)} d_0 + d_1)}. \quad (109)$$

Thus, the system behaves essentially as the two level system discussed in Examples 4.4 and 8.5; the **spectral gap**  $E_1 - E_0$  takes the role of  $E$ . In particular, if already  $kT \ll E_1 - E_0$ , we find that

$$e^{-S/k} = d_0^{-1} P_0 + O(e^{-\beta(E_1 - E_0)}) \approx d_0^{-1} P_0 \quad (\text{if } kT \ll E_1 - E_0)$$

is essentially the projector to the subspace of minimal energy, scaled to ensure trace one.

In the **nondegenerate** case, where the lowest energy eigenvalue is simple, there is a corresponding normalized eigenvector  $\psi$ , unique up to a phase, satisfying the **Schrödinger equation**

$$H\psi = E_0\psi, \quad |\psi| = 1 \quad (E_0 \text{ minimal}). \quad (110)$$

In this case, the projector is  $P_0 = \psi\psi^*$  and has rank  $d_0 = 1$ . Thus

$$e^{-S/k} = \psi\psi^* + O(e^{-\beta(E_1 - E_0)}).$$

has almost rank one, and the value takes the form

$$\langle g \rangle = \text{tr} e^{-S/k} g \approx \text{tr} \psi\psi^* g = \psi^* g \psi. \quad (111)$$

In the terminology of quantum mechanics,  $E_0$  is the **ground state energy**, the solution  $\psi$  of (110) is called the **ground state**, and  $\langle g \rangle = \psi^* g \psi$  is the expectation of the observable  $g$  in the ground state.



Our derivation therefore shows that – unless the ground state is degenerate – *a canonical ensemble at sufficiently low temperature is in an almost pure state described by the quantum mechanical ground state.*

Thus, the third law directly leads to the conventional form of quantum mechanics, which can therefore be understood as the low temperature limit of thermodynamics. It also indicates when a quantum mechanical description by a pure state is appropriate, namely always when the gap between the ground state energy and the next energy level is significantly larger than the temperature, measured in units of the Boltzmann constant. (This is the typical situation in most of quantum chemistry and justifies the use of the Born-Oppenheimer approximation in the absence of level crossing; cf. SMITH [116], YARKONY [133]). Moreover, it gives the correct (mixed) form of the state in case of ground state degeneracy, and the form of the correction terms when the energy gap is not large enough for the ground state approximation to be valid.

It is remarkable that thermodynamics in this way predicts the Schrödinger equation, the relevance of the spectrum of the Hamiltonian, and the formula for quantum expectations in a pure state. Indeed, after adding suitable dynamical assumptions, it is possible to interpret all quantum mechanics from this point of view. The resulting **thermal interpretation** of quantum mechanics will be discussed in NEUMAIER [95].

### 13 Local, microlocal, and quantum equilibrium

As we have seen in Section 9, when descriptions on several levels are justified empirically, they differ significantly only in quantities which are negligible in the more detailed models, or by terms which are not observable in principle. Thus, the global equilibrium description is adequate at some resolution if and only if only small nonequilibrium forces are present, and a more detailed local equilibrium description will (apart from variations of the Gibbs paradox which should be cured on the more detailed level) agree with the global equilibrium description to the accuracy within which the differences in the corresponding approximations to the entropy, as measured by the relative entropy (50), are negligible. Of course, if the relative entropy of a thermal state relative to the true Gibbs state is large then the thermal state cannot be regarded as a faithful description of the true state of the system, and the thermal model is inadequate.

In statistical mechanics proper (where the microscopic dynamics is given), the relevant extensive quantities are those whose values vary slowly enough to be macroscopically observable at a given spatial or temporal resolution (cf. BALIAN [8]). Which ones must be included is a difficult mathematical problem which has been solved only in simple situations (such as monatomic gases) where a weak coupling limit applies. In more general situations, the selection is currently based on phenomenological consideration, without any formal mathematical support.

In equilibrium statistical mechanics, which describes time-independent, *global* equilibrium situations, the relevant extensive quantities are the additive conserved quantities of a microscopic system and additional parameters describing order parameters that emerge from broken symmetries or various defects not present in the ideal model. **Phase equilibrium** needs, in addition, copies of the extensive variables (e.g., partial volumes) for each phase, since the phases are spatially distributed, while the intensive variables are shared by all phases. **Chemical equilibrium** also accounts for exchange of atoms through a fixed list of permitted chemical reactions whose length is again determined by the desired resolution.

In states not corresponding to global equilibrium – usually called **non-equilibrium states**, a thermal description is still possible assuming so-called **local equilibrium**. There, the natural extensive quantities are those whose values are locally additive and slowly varying in space and time and hence, reliably observable at the scales of interest. In the statistical mechanics of local equilibrium, the thermal variables therefore become space- and time-dependent fields (ROBERTSON [110]). On even shorter time scales, phase space behavior becomes relevant, and the appropriate description is in terms of **microlocal equilibrium** and position- and momentum-dependent phase space densities. Finally, on the microscopic level, a linear operator description in terms of **quantum equilibrium** is needed.

The present formalism is still applicable to local, microlocal, and quantum equilibrium (though most products now become inner products in suitable function spaces), but the relevant quantities are now time-dependent and additional dynamical issues (relating states at different times) arise which are outside the scope of the present paper.

In local equilibrium, one needs a hydrodynamic description by Navier-Stokes equations and their generalizations; see, e.g., BERIS & ESWARDS [16], OETTINGER [97], EDWARDS et al. [38]. In the local view, one gets the interpretation of extensive variables as locally conserved (or at least slowly varying) quantities (whence additivity) and of intensive variables as parameter fields, which cause non-equilibrium currents when they are not constant, driving the system towards global equilibrium. In microlocal equilibrium, one needs a kinetic description by the Boltzmann equation and its generalizations; see, e.g., BORNATH et al. [21], CALZETTA & HU [27], MÜLLER & RUGGERI [90].

**Quantum equilibrium.** Full microscopic dynamics must be based on quantum mechanics. In quantum equilibrium, the dynamics is given by quantum dynamical semigroups. We outline the ideas involved, in order to emphasize some issues which are usually swept under the carpet.

Even when described at the microscopic level, thermal systems of sizes handled in a laboratory are in contact with their environment, via containing walls, emitted or absorbed radiation, etc.. We therefore embed the system of interest into a bigger, completely isolated system and assume that the quantum state of the big system is described at a fixed time by a normalized wave function  $\psi$  in some Hilbert space  $\mathbb{H}$ . (Assuming instead a mixed state

given by a density operator would not alter the picture significantly.) The value of a linear operator  $g$  in the big system is

$$\langle g \rangle = \psi^* g \psi; \quad (112)$$

cf. (111). The small system is defined by a Euclidean  $*$ -algebra  $\mathbb{E}$  of linear operators densely defined on  $\widehat{\mathbb{H}}$ , composed of all meaningful expressions in field operators at arguments in the region of interest, with integral given by the trace in the big system. Since (112), restricted to  $g \in \mathbb{E}$ , satisfies the rules (R1)–(R4) for a state, the big system induces on the system of interest a state. By standard theorems (see, e.g., THIRRING [122]), there is a unique **density operator**  $\rho \in \mathbb{E}$  such that  $\langle g \rangle = \int \rho g$  for all  $g \in \mathbb{E}$  with finite value. Moreover,  $\rho$  is Hermitian and positive semidefinite. If 0 is not an eigenvalue of  $\rho$  (which will usually be the case), then  $\langle \cdot \rangle$  is a Gibbs state with entropy  $S = -k \log \rho$ . To put quantum equilibrium into the thermal setting, we need to choose as extensive variables a family spanning the algebra  $\mathbb{E}$ ; then each such  $S$  can be written in the form (54).

Of course,  $\psi$  and hence the state  $\langle \cdot \rangle$  depend on time. If the reduced system were governed by a Schrödinger equation then  $\rho$  would evolve by means of a unitary evolution; in particular,  $\overline{S} = \langle S \rangle = -k \operatorname{tr} \rho \log \rho$  would be time-independent. However, the system of interest does *not* inherit a Schrödinger dynamics from the isolated big system; rather, the dynamics of  $\rho$  is given by an integro-differential equation with a complicated memory term, defined by the projector operator formalism described in detail in GRABERT [50]; for summaries, see RAU & MÜLLER [105] and BALIAN [8]. In particular, one can say nothing specific about the dynamics of  $\overline{S}$ .

In typical treatments of such reduced descriptions, one assumes that the memory decays sufficiently fast; this so-called **Markov assumption** can be justified in a weak coupling limit (DAVIES [37], SPOHN [117]), which corresponds to a system of interest nearly independent of the environment. But a typical thermal system, such as a glass of water on a desk is held in place by the container. Considered as a nearly independent system, the water would behave very differently, probably diffusing into space. Thus, it is questionable whether the Markov assumption is satisfied; a detailed investigation of the situation would be highly desirable. I only know of few discussions of the problem how containers modify the dynamics of a large quantum system; see, e.g., LEBOWITZ & FRISCH [79], BLATT [18] and RIDDERBOS [108]. One should expect a decoherence effect (BRUNE et al. [24]) of the environment on the system which, for large quantum systems, is extremely strong (ZUREK [134]). A fundamental derivation should be based on quantum field theory; the so-called exact renormalization group equations (see, e.g., POLONYI & SAILER [102], BERGES [14]) have a thermal flavor and might be a suitable starting point.

However, simply assuming the Markov assumption as the condition for regarding the system of interest to be **effectively isolated** allows one to deduce for the resulting **Markov approximation** a deterministic differential equation for the density operator. The dynamics then describes a linear quantum dynamical semigroup. All known linear quantum dynamical semigroups (cf. DAVIES [37]) on a Hilbert space correspond to a dynamics

in the form of a **Lindblad equation**

$$\dot{\rho} = \frac{i}{\hbar}(\rho H - H^* \rho) + P^* \rho \quad (113)$$

(LINDBLAD [81], GORINI et al. [49]), where the **effective Hamiltonian**  $H$  is a not necessarily Hermitian operator and  $P^*$  is the dual of a completely positive map of the form

$$P(f) = Q^* J(f) Q \quad \text{for all } f \in \mathbb{E},$$

with some linear operator  $Q$  from  $\mathbb{E}$  to a second \*-algebra  $\mathbb{E}'$  and some \*-algebra homomorphism  $J$  from  $\mathbb{E}$  to  $\mathbb{E}'$ . (STINESPRING [119], DAVIES [37, Theorem 2.1]). Their dynamics is inherently dissipative; for time  $t \rightarrow \infty$ ,  $P^* \rho$  tends to zero, which usually implies that, apart from a constant velocity, the limiting state is a global equilibrium state.

Thus, the irreversibility of the time evolution is apparent already at the quantum level, being caused by the fact that all our observations are done in a limited region of space. The prevalence here on earth of matter in approximate equilibrium could therefore possibly be explained by the fact that the earth and with it most of its materials are extremely old.

For a system reasonably isolated (in the thermodynamical sense) from its environment, one would expect  $H$  to contain a confining effective potential well and  $P$  to be small. It would be interesting to understand the conditions (if there are any) under which the dissipation due to  $P$  can be neglected.

We now consider relations within the hierarchy of the four levels. The quantum equilibrium entropy  $S_{\text{qu}}$ , the microlocal equilibrium entropy  $S_{\text{ml}}$ , the local equilibrium entropy  $S_{\text{lc}}$ , the global equilibrium entropy  $S_{\text{gl}}$  denote the values of the entropy in a thermal description of the corresponding equilibrium levels. The four levels have a more and more restricted set of extensive quantities, and the relative entropy argument of Theorem 5.3 can be applied at each level. Therefore

$$S_{\text{qu}} \leq S_{\text{ml}} \leq S_{\text{lc}} \leq S_{\text{gl}}. \quad (114)$$

In general the four entropies might have completely different values. There are four essentially different possibilities,

- (i)  $S_{\text{qu}} \approx S_{\text{ml}} \approx S_{\text{lc}} \approx S_{\text{gl}}$ ,
- (ii)  $S_{\text{qu}} \approx S_{\text{ml}} \approx S_{\text{lc}} \ll S_{\text{gl}}$ ,
- (iii)  $S_{\text{qu}} \approx S_{\text{ml}} \ll S_{\text{lc}} \leq S_{\text{gl}}$ ,
- (iv)  $S_{\text{qu}} \ll S_{\text{ml}} \leq S_{\text{lc}} \leq S_{\text{gl}}$ ,

with different physical interpretations. As we have seen in Section 9, a thermal description is valid only if the entropy in this description approximates the true entropy sufficiently well. All other entropies, when significantly different, do not correspond to a correct description

of the system; their disagreement simply means failure of the coarser description to match reality. (Again, we disregard variations of the Gibbs paradox which should be cured on the fundamental level.) Thus which of the cases (i)–(iv) occurs decides upon which descriptions are valid. (i) says that the state is in global equilibrium, and all four descriptions are valid. (ii) that the state is in local, but not in global equilibrium, and only the three remaining descriptions are valid. (iii) says that the state is in microlocal, but not in local equilibrium, and in particular not in global equilibrium. Only the basic and the microlocal descriptions are valid. Finally, (iv) says that the state is not even in microlocal equilibrium, and only the quantum description is valid.

Thus (assuming that the fundamental limitations in obserability are correctly treated on the quantum level), the entropy is an objective quantity, independent of the level of accuracy with which we are able to describe the system, although the precise value it gets in a model of course depends on the accuracy of the model. The observation (by GRAD [51], BALIAN [8], and others) that entropy may depend significantly on the description level is explained by two facts which hold for models of any kind, not just for entropy, namely:

- (i) that if two models disagree in their predictions, at most one one of them can be correct, and
- (ii) that if two models agree in their predictions, the more detailed model has unobservable details.

Since unobservable details cannot be put to an experimental test, the more detailed model in case (ii) is questionable unless dictated by fundamental considerations of formal simplicity.

## A Appendix: Entropy and unobservable complexity

The concept of entropy is usually introduced either historically by the Carnot cycle and an assumed informal form of the second law of thermodynamics, or, following a more recent (1957) subjectivistic approach (JAYNES [62, 63]), by the information available to an observer and the second law in form of the principle of maximum entropy.

In our treatment, we avoided both, rejecting them as being principles that require explanation themselves. The Carnot cycle is clearly inappropriate in a foundational setting, and a subjectivist approach is inappropriate for the description of a world that existed long before there were human observers.

However, to connect the traditional approach with the present setting, we present in this section an informal example of a simple stochastic model in which the entropy indeed has an information theoretical interpretation and then discuss what this can teach us about a probability-free macroscopic view of the situation.

Suppose that we have a simple stationary device which, in regular intervals, delivers a reading  $n$  from a countable set  $\mathcal{N}$  of possible readings. For example, the device might count

the number of events of a certain kind in fixed periods of time; then  $\mathcal{N} = \{0, 1, 2, \dots\}$ .

We suppose that, by observing the device in action for some time, we are led to some conjecture about the (expected) relative frequencies  $p_n$  of readings  $n \in \mathcal{N}$ ; since the device is stationary, these relative frequencies are independent of time. (If  $\mathcal{N}$  is finite and not too large, we might take averages and wait until these stabilize to a satisfactory degree; if  $\mathcal{N}$  is large or infinite, most  $n \in \mathcal{N}$  will not have been observed, and our conjecture must depend on educated guesses. This introduces some subjectiveness and is the reason why the following material is deferred to an appendix.)

Clearly, in order to have a consistent interpretation of the  $p_n$  as relative frequencies, we need to assume that *each* reading is possible:

$$p_n > 0 \text{ for all } n \in \mathcal{N}, \quad (115)$$

and *some* reading occurs with certainty:

$$\sum_{n \in \mathcal{N}} p_n = 1. \quad (116)$$

(For reasons of economy, we shall not allow  $p_n = 0$  in (115), which would correspond to readings that are either impossible, or occur too rarely to have a scientific meaning. Clearly, this is no loss of generality.) Knowing relative frequencies only means that (when  $\mathcal{N} > 1$ ) we only have incomplete information about future readings of the device. We want to calculate the information deficit by counting the expected number of questions needed to identify a particular reading unknown to us, but known to someone else who may answer our questions with yes or no.

Consider an arbitrary strategy for asking questions, and denote by  $s_n$  the number of questions needed to determine the reading  $n$ . With  $q$  questions we can distinguish up to  $2^q$  different cases; but since reading  $n$  is already determined after  $s_n$  questions, reading  $n$  is obtained in  $2^{q-s_n}$  of the  $2^q$  cases (when  $s_n \leq q$ ). Thus

$$\sum_{s_n \leq q} 2^{q-s_n} \leq 2^q.$$

If we divide by  $2^q$  and then make  $q$  arbitrarily large we find that

$$\sum_{n \in \mathcal{N}} 2^{-s_n} \leq 1. \quad (117)$$

It is not difficult to construct strategies realizing the  $s_n$  whenever (117) holds.

Since we do not know in advance the reading, we cannot determine the precise number of questions needed in a particular unknown case. However, knowledge of the relative frequencies allows us to compute the average number of questions needed, namely

$$\bar{s} = \sum_{n \in \mathcal{N}} p_n s_n. \quad (118)$$

To simplify notation, we introduce the abbreviation

$$\int f := \sum_{n \in \mathcal{N}} f_n \quad (119)$$

for every quantity  $f$  indexed by the elements from  $\mathcal{N}$ , and we use the convention that inequalities, operations and functions of such quantities are understood componentwise. Then we can rewrite (115)–(118) as

$$p > 0, \quad \int p = 1, \quad (120)$$

$$\bar{s} = \int p s, \quad \int 2^{-s} \leq 1, \quad (121)$$

and

$$\bar{f} = \langle f \rangle := \int p f. \quad (122)$$

is the average of an arbitrary quantity  $f$  indexed by  $\mathcal{N}$ .

We now ask for a strategy which makes the number  $\bar{s}$  as small as possible. However, we idealize the situation a little by allowing the  $s_n$  to be arbitrary nonnegative real numbers instead of integers only. This is justified when the size of  $\mathcal{N}$  is large or infinite since then most  $s_n$  will be large numbers which can be approximated by integers with a tiny relative error.

**A.1 Theorem.** *The entropy  $S$ , defined by*

$$S := -\bar{k} \log p, \quad \text{where } \bar{k} = \frac{1}{\log 2}, \quad (123)$$

*satisfies  $\bar{S} \leq \bar{s}$ , with equality if and only if  $s = S$ .*

*Proof.* (123) implies  $\log p = -S \log 2$ , hence  $p = 2^{-S}$ . Therefore

$$2^{-s} = p 2^{S-s} = p e^{\log 2(S-s)} \geq p(1 + \log 2(S-s)),$$

with equality iff  $S = s$ . Thus

$$p(S-s) \leq \frac{1}{\log 2}(2^{-s} - p) = \bar{k}(2^{-s} - p)$$

and

$$\begin{aligned} \bar{S} - \bar{s} &= \int p(S-s) \leq \int \bar{k}(2^{-s} - p) \\ &= \bar{k} \int 2^{-s} - \bar{k} \int p \leq \bar{k} - \bar{k} = 0. \end{aligned}$$

Hence  $\bar{s} \geq \bar{S}$ , and equality holds iff  $s = S$ . □

Since (123) implies the relation  $p = e^{-S/k}$ , we have  $\langle f \rangle = \int p f = \int e^{-S/k} f$ . Thus, the expectation mapping is a Gibbs state with entropy  $S$ , explaining the name. Note that  $s = S$  defines an admissible strategy since

$$\sum_{n \in \mathcal{N}} 2^{-S_n} = \int 2^{-S} = \int p = 1,$$

hence  $2^{-S_n} \leq 1$ ,  $S_n \geq 0$  for all  $n \in \mathcal{N}$ . Thus, the entropy  $S$  is **the unique optimal decision strategy**. The **expected entropy**, i.e., the mean number

$$\bar{S} = \langle S \rangle = \int p S = -k \int p \log p \quad (124)$$

of questions needed in an optimal decision strategy, is nonnegative,

$$\bar{S} \geq 0. \quad (125)$$

It measures the **information deficit** of the device with respect to our conjecture about relative frequencies. (Traditionally, this is simply called the entropy, while we reserve this word for the random variable (123). Also commonly used is the name *information* for  $\bar{S}$ , which invites linguistic paradoxes since ordinary language associates with information a connotation of relevance or quality which is absent here. An important book on information by BRILLOUIN [23] emphasizes this very carefully, by distinguishing absolute information from its human value or meaning. KATZ [70] uses the phrase 'missing information'.)

The information deficit says nothing at all about the quality of the information contained in the summary  $p$  of our past observations. An inappropriate  $p$  can have arbitrarily small information deficit and still give a false account of reality. E.g., if for some small  $\varepsilon > 0$ ,

$$p_n = \varepsilon^{n-1}(1 - \varepsilon) \quad \text{for } n = 1, 2, \dots, \quad (126)$$

expressing that the reading is expected to be nearly always 1 ( $p_1 = 1 - \varepsilon$ ) and hardly ever large, then

$$\bar{S} = k \left( \log(1 - \varepsilon) + \frac{\varepsilon}{1 - \varepsilon} \log \varepsilon \right) \rightarrow 0 \text{ as } \varepsilon \rightarrow 0.$$

Thus the information deficit can be made very small by the choice (126) with small  $\varepsilon$ , independent of whether this choice corresponds to the known facts. The real information value of  $p$  depends instead on the care with which the past observations were interpreted, which is a matter of data analysis and not of our model of the device. If this is done badly, our expectations will simply not be matched by reality. This shows that the entropy has nothing to do with "our knowledge of the system" – a subjective, ill-defined notion – but reflects objective properties of the stochastic process.

**Relations to thermodynamics.** Now suppose that the above setting happens at a very fast, unobservable time scale, so that we can actually observe only short time averages



(122) of quantities of interest. Then  $\bar{f} = \langle f \rangle$  simply has the interpretation of the time-independent observed value of the quantity  $f$ . The information deficit simply becomes the observed value of the entropy  $S$ . Since the information deficit counts the number of optimal decisions needed to completely specify a (microscopic) situation of which we know only (macroscopic) observed values, the observed value of the entropy quantifies the **intrinsic** (microscopic) **complexity** present in the system.

However, the unobservable high frequency fluctuations of the device do not completely disappear from the picture. They show in the fact that generally  $\overline{g^2} \neq \bar{g}^2$ , leading to a nonzero limit resolution (53) of Hermitian quantities. This is precisely the situation characteristic of the traditional treatment of thermodynamics within classical equilibrium statistical mechanics, if we assume *ergodicity*, i.e., that ensemble averages equal time averages. (This is a problematic assumption; see, e.g., the discussion in SKLAR [115].) There, all observed values are time-independent, described by equilibrium thermal variables. But the underlying high-frequency motions of the atoms making up a macroscopic substance are revealed by nonzero limit resolutions.

Note that even a deterministic but chaotic high frequency dynamics, viewed at longer time scales, looks stochastic, and exactly the same remarks about the unobservable complexity and the observable consequences of fluctuations apply. Even if fluctuations are observable directly, these observations are intrinsically limited by the necessary crudity of any actual measurement protocol. For the best possible measurements (and only for these), the resolution of  $f$  in the experiment is given by the limit resolution  $\text{Res}(f)$ , the size of the unavoidable fluctuations.

Due to the quantum structure of high frequency phenomena (on an atomic or subatomic scale), it may, however, seem problematic to interpret the thermodynamic limit resolutions in terms of a simple short time average of some underlying microscopic reality. Fortunately, as we have seen, such an interpretation is not necessary.

## B Appendix: The maximum entropy principle

Motivated by a subjective, information theoretic approach to probability, JAYNES ([62] for the classical case and [63] for the quantum case), used the maximum entropy principle to derive the thermal formalism. This approach has gained considerable acceptance in the physics community. But why should nature be concerned about the the amount of information an observer has? According to whose knowledge should it behave? Since thermodynamics is completely observer independent, its foundations should have this feature, too.

The present approach avoids this subjective touch and shows that a fully objective foundation is possible. The maximum entropy principle becomes a theorem, valid (only) under

precisely specified conditions. To denote the extensive variables, we use the barless notation of Section 2.

**B.1 Theorem. (Entropy form of the second law)**

*In an arbitrary state of a standard thermal system*

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

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

$$T^{-1} = \frac{\partial S}{\partial H}(H, V, N), \quad T^{-1}P = \frac{\partial S}{\partial V}(H, V, N), \quad T^{-1}\mu = -\frac{\partial S}{\partial N}(H, V, N), \quad (127)$$

$$U = H = TS(T, V, N) - PV + \mu \cdot N. \quad (128)$$

*Proof.* This is proved in the same way as Theorem 3.2; thus we give no details. □

The *only* situation in which the value of the entropy *must* increase to reach equilibrium is when  $H$ ,  $V$  and  $N$  are kept constant. Under different constraints, the entropy is no longer maximal. For example, if one pours milk into one's 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 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 particle number, the value of the entropy decreases when  $\bar{H}$  or  $V$  (or both) decrease reversibly; this shows that the value of the entropy may well decrease if accompanied by a corresponding decrease of  $\bar{H}$  or  $V$ . The same holds out of equilibrium (though our argument no longer applies); for example, the reaction  $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$  (if catalyzed) may happen spontaneously at constant  $T = 25^\circ\text{C}$  and  $P = 1 \text{ atm}$ , though it decreases the entropy.

The conditions of constant  $H$ ,  $V$  and  $N$ , needed to argue that entropy must increase, are not easily realized in nature. From a fundamental point of view, they are even always violated: The only truly isolated system is the universe as a whole; but the universe expands, i.e.,  $V$  changes. Thus, the assumption of constant  $H$ ,  $V$  and  $N$  is unrealistic, and while the second law in the form of a maximum entropy principle may be of theoretical and historical importance, it is not the extremal principle ruling nature.

The irreversible nature of physical processes is instead manifest, irrespective of the entropy balance, as energy dissipation which, in a microscopic interpretation, indicates the loss of energy to the unmodelled microscopic degrees of freedom. 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.)

The maximum entropy principle is also heralded as an rational, unprejudiced way of accounting for available information in incompletely known statistical models. However, it accounts only for information about exact expectation values, and the model produced by the maximum entropy principle describes the true situation correctly only if the expectations of the sufficient statistics of the true model are available exactly; see, e.g., BARNDORFF-NIELSEN [11]. Which statistics can be considered sufficient depends on the true situation and is difficult to assess in advance. The maximum entropy principle amounts in this situation simply to the (often unfounded) assumption that the sufficient statistics are among the quantities of which one happens to know the expectation values. Moreover, questions about the uninformative prior which must be assumed to describe the state of complete ignorance affect the results of the maximum entropy principle, making the application of the principle ambiguous.

**B.2 Examples.** (i) If we have information in the form of a large but finite sample of  $N$  realizations  $g(\Omega_k)$  ( $k = 1, \dots, n$ ) of a random variable  $g$ , we can obtain from it approximate information about all moments  $\langle g^n \rangle \approx \sum g(\Omega_k)^n / N$  ( $n = 0, 1, 2, \dots$ ). The maximum entropy principle would infer that the distribution of  $g$  is discrete, namely that of the sample.

(ii) If we take as uninformative prior for a real-valued random variable  $g$  the Lebesgue measure and only know that the mean of  $g$  is 1, the maximum entropy principle does not produce a sensible probability distribution. If we add the knowledge of the second moment  $\langle g^2 \rangle = 2$ , we get a Gaussian distribution with mean 1 and standard deviation 1. If we then get to know that the random variable is in fact nonnegative and integer-valued, this cannot be accounted for by the principle, and the probability of obtaining a negative value remains large.

(iii) But if we take as prior the discrete measure on nonnegative integers, the 'noninformative' prior has become much more informative, the knowledge of the mean produces the Poisson distribution, and the knowledge of the second moment may modify this further.

(iv) If we know that a random variable  $g$  is nonnegative and has  $\langle g^2 \rangle = 1$ ; the Lebesgue measure on  $\mathbb{R}_+$  as noninformative prior gives for  $g$  a distribution with density  $\sqrt{2/\pi}e^{-g^2/2}$ . But we can consider instead our knowledge about  $h = g^2$ , which is nonnegative and has  $\langle h \rangle = 1$ ; the same noninformative prior now gives for  $h$  a distribution with density  $e^{-h}$ . The distribution of  $g = \sqrt{h}$  resulting from this has density  $2ge^{-g^2/2}$ . Thus the result depends on whether we regard  $g$  or  $h$  as the relevant variable.

These examples clearly demonstrate that the maximum entropy principle is an unreliable tool. The prior, far from being uninformative, reflects the prejudice assumed without any knowledge, and the choice of expectations to use reflects prior experience about which expectations are likely to be relevant. Thus the application of the maximum entropy principle becomes reliable only if one knows the desired for mof the result beforehand (which was indeed the case with Jaynes' arguments, many years after Gibbs). Thus, the principle is not a suitable basis for the foundations of thermodynamics.

## C Appendix: Some mathematical lemmas

In this section we prove some mathematical results needed in the main text. The proofs are rigorous for the case  $\mathbb{E} \subseteq \mathbb{C}^{n \times n}$  only; this covers the  $N$ -level quantum system, but also quantum field theory in the finite lattice approximation, and implies the results whenever  $\mathbb{E}$  is finite-dimensional. Similar arguments work in more general situations if we use spectral resolutions; cf., e.g., THIRRING [122] (who works in  $C^*$ -algebras and von Neumann algebras). I'd appreciate to be informed about possible proofs in general that only use the properties of Euclidean  $*$ -algebras (and perhaps further, elementary assumptions).

**C.1 Proposition.** *For arbitrary quantities  $f, g$ ,*

$$\begin{aligned} e^{\alpha f} e^{\beta f} &= e^{(\alpha+\beta)f} \quad (\alpha, \beta \in \mathbb{R}), \\ (e^f)^* &= e^{f^*}, \\ e^f g &= g e^f \quad \text{if } f \text{ and } g \text{ commute,} \\ f^* &= f \quad \Rightarrow \quad \log e^f = f, \\ f \geq 0 &\quad \Rightarrow \quad \sqrt{f} \geq 0, \quad (\sqrt{f})^2 = f, \end{aligned}$$

For any quantity  $f = f(s)$  depending continuously on  $s \in [a, b]$ ,

$$\int_a^b ds \int f(s) = \int \left( \int_a^b ds f(s) \right),$$

and for any quantity  $f = f(\lambda)$  depending continuously differentiable on a parameter vector  $\lambda$ ,

$$\frac{d}{d\lambda} \int f = \int df/d\lambda.$$

*Proof.* In finite dimensions, the first four assertions are standard matrix calculus, and the remaining two statements hold since  $\int f$  must be a finite linear combination of the components of  $f$ .  $\square$

**C.2 Proposition.** *Let  $f, g$  be quantities depending continuously differentiable on a parameter vector  $\lambda$ , and suppose that*

$$[f(\lambda), g(\lambda)] = 0 \text{ for all } \lambda.$$

Thus, for any continuously differentiable function  $F$  of two variables,

$$\frac{d}{d\lambda} \int F(f, g) = \int \partial_1 F(f, g) \frac{df}{d\lambda} + \int \partial_2 F(f, g) \frac{dg}{d\lambda}. \quad (129)$$

*Proof.* We prove the special case  $F(x, y) = x^m y^n$ , where (129) reduces to

$$\frac{d}{d\lambda} \int f^m g^n = \int m f^{m-1} g^n \frac{df}{d\lambda} + \int n f^m g^{n-1} \frac{dg}{d\lambda}. \quad (130)$$

The general case then follows for polynomials  $F(x, y)$  by taking suitable linear combinations, and for arbitrary  $F$  by a limiting procedure. To prove (130), we note that, more generally,

$$\begin{aligned} \frac{d}{d\lambda} \int f_1 \cdots f_{m+n} &= \int \frac{d}{d\lambda} (f_1 \cdots f_{m+n}) \\ &= \int \sum_{j=1}^{m+n} f_1 \cdots f_{j-1} \frac{df_j}{d\lambda} f_{j+1} \cdots f_{m+n} \\ &= \sum_{j=1}^{m+n} \int f_1 \cdots f_{j-1} \frac{df_j}{d\lambda} f_{j+1} \cdots f_{m+n} \\ &= \sum_{j=1}^{m+n} \int f_{j+1} \cdots f_{m+n} f_1 \cdots f_{j-1} \frac{df_j}{d\lambda}, \end{aligned}$$

using the cyclic commutativity (EA2) of the integral. If we specialize to  $f_j = f$  if  $j \leq m$ ,  $f_j = g$  if  $j > m$ , and note that  $f$  and  $g$  commute, we arrive at (130).  $\square$

Of course, the proposition generalizes to families of more than two commuting quantities; but more important is the special case  $g = f$ :

**C.3 Corollary.** *For any quantity  $f$  depending continuously differentiablely on a parameter vector  $\lambda$ , and any continuously differentiable function  $F$  of a single variable,*

$$\frac{d}{d\lambda} \int F(f) = \int F'(f) \frac{df}{d\lambda}. \quad (131)$$

A real-valued function  $\phi$  is convex in a convex set  $X \subseteq \mathbb{R}^n$  if  $\phi$  is defined on  $X$  and, for all  $x, y \in X$ ,

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

Clearly,  $\phi$  is convex iff for all  $x, y \in X$ , the function  $\mu : [0, 1] \rightarrow \mathbb{R}$  defined by

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

is convex. It is well-known that, for twice continuously differentiable  $\phi$ , 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 [2], FRANKLIN [46], ROCKAFELLAR [112]), convex functions are almost everywhere twice continuously differentiable, in the sense that, for every  $x \in X$ , there exist a gradient vector  $\frac{\partial}{\partial x} \phi(x) \in \mathbb{R}^n$  and a symmetric, positive definite Hessian matrix  $\frac{\partial^2}{\partial x^2} \phi(x) \in \mathbb{R}^{n \times n}$  such that, for arbitrary  $h \in \mathbb{R}^n$ ,

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

A function  $\phi$  is concave iff  $-\phi$  is convex. Thus, for twice continuously differentiable  $\phi$ ,  $\phi$  is concave iff  $\mu''(t) \leq 0$  for  $0 \leq t \leq 1$ .

**C.4 Proposition.** *If  $\phi$  is convex then the function  $\psi$  defined by*

$$\psi(s, x) := s\phi(x/s)$$

*is convex for  $s > 0$  and concave for  $s < 0$ .*

*Proof.* It suffices to show that  $\mu(t) := \psi(s + tk, x + th)$  is convex (concave) for all  $s, x, h, k$  such that  $s + tk > 0$  (resp.  $< 0$ ). Let  $z(t) := (x + th)/(s + tk)$  and  $c := sh - kx$ . Then

$$z'(t) = \frac{c}{(s + tk)^2}, \quad \mu(t) = (s + tk)\phi(z(t)),$$

hence

$$\begin{aligned} \mu'(t) &= k\phi(z(t)) + \phi'(z(t))\frac{c}{s + tk}, \\ \mu''(t) &= k\phi'(z(t))\frac{c}{(s + tk)^2} + \frac{c^T}{(s + tk)^2}\phi''(z(t))\frac{c}{s + tk} + \phi'(z(t))\frac{-ck}{(s + tk)^2} = \frac{c^T\phi''(z(t))c}{(s + tk)^3}, \end{aligned}$$

which has the required sign.  $\square$

## References

- [1] R.A. Alberty, Use of Legendre transforms in chemical thermodynamics (IUPAC Technical Report), Pure Appl. Chem. 73 (2001), 1349–1380.
- [2] A.D. Aleksandrov, Almost everywhere existence of the second differential of a convex function and some properties of convex surfaces connected with it (in Russian), Leningrad State Univ. Ann. Math. Ser. 6 (1939), 3–35.
- [3] Y. Alhassid and R. D. Levine, Connection between the maximal entropy and the scattering theoretic analyses of collision processes, Phys. Rev. A 18 (1978), 89–116.
- [4] A.E. Allahverdyan and T.M. Nieuwenhuizen, Explanation of the Gibbs paradox within the framework of quantum thermodynamics, Phys. Rev. E 73 (2006), 066119.
- [5] T. Andrews, The Bakerian Lecture: On the Continuity of the Gaseous and Liquid States of Matter Phil. Trans. Royal Soc. London 159 (1869), 575–590.
- [6] V.I. Arnol'd, Mathematical Methods of Classical Mechanics, Springer, New York 1989.

- [7] R. Balian, *From Microphysics to Macrophysics: Methods and Applications of Statistical Physics*, Vol. II, Springer, Berlin 2007.
- [8] R. Balian, Incomplete descriptions and relevant entropies *Amer. J. Phys.* 67 (1999), 1078–1090.
- [9] R. Balian, Information in statistical physics, *Studies in History and Philosophy of Modern Physics* 36 (2005), 323–353. cond-mat/0501322
- [10] L. E. Ballentine, *The Statistical Interpretation of Quantum Mechanics*, *Rev. Mod. Phys.* 42 (1970), 358–381.
- [11] O. Barndorff-Nielsen, *Information and exponential families in statistical theory*, Wiley, Chichester 1978.
- [12] O.E Barndorff-Nielsen, R.D. Gill and P.E. Jupp, On quantum statistical inference, *J. Roy. Statist. Soc. B* 65 (2003), 1–31. quant-ph/0307191
- [13] R. Battino, L.E. Strong, and S.E. Wood, A Brief History of Thermodynamics Notation, *J. Chem. Education* 74 (1997), 304–305.
- [14] J. Berges, Introduction to nonequilibrium quantum field theory, *AIP Conf. Proc.* 739 (2004), 3–62. hep-ph/0409233
- [15] J. Berges, N. Tetradis and C. Wetterich, Non-Perturbative Renormalization Flow in Quantum Field Theory and Statistical Physics, *Phys. Rep.* 363 (2002), 223–386. hep-ph/0005122
- [16] A.N. Beris and B.J. Edwards, *Thermodynamics of flowing systems with internal microstructure*, Oxford Univ. Press, New York 1994.
- [17] J.M. Bernardo and A.F.M. Smith, *Bayesian theory*, Wiley, Chichester 1994.
- [18] J.M. Blatt, An Alternative Approach to the Ergodic Problem, *Prog. Theor. Phys.* 22 (1959), 745–756.
- [19] N.N. Bogoliubov, On a variational principle in the problem of many bodies (in Russian), *Dokl. Akad. Nauk SSSR* 119 (1958), 244–246. See also J. Kvasnikov, On the application of a variational principle to the Ising model of ferromagnetism (in Russian), *Dokl. Akad. Nauk SSSR* 110 (1956), 755–757.
- [20] Bonhoeffer and P. Harteck, Para- and ortho hydrogen, *Z. Physikalische Chemie B* 4 (1929), 113–141.
- [21] T. Bornath, D. Kremp, W.D. Kraeft and M. Schlanges, Kinetic equations for a nonideal quantum system, *Phys. Rev. E* 54 (1996), 3274–3284.

- [22] F.P. Bowden and L. Leben, The nature of sliding and the analysis of friction, Proc Royal Society London. Series A 169 (1939), 371–391.
- [23] L. Brillouin, Science and Information Theory. 2nd ed., Acad. Press, New York 1962.
- [24] M. Brune et al., Observing the progressive decoherence of the “meter” in a quantum measurement, Phys. Rev. Lett. 77 (1996), 4887–4890.
- [25] C. Bustamente, J. Liphardt and F. Ritort, The nonequilibrium thermodynamics of small systems, Physics Today 58 (2005), 43–48. cond-mat/0511629
- [26] H.B. Callen, Thermodynamics and an introduction to thermostatistics, 2nd. ed., Wiley, New York 1985
- [27] E. Calzetta and B.L. Hu, Nonequilibrium quantum fields: Closed-time-path effective action, Wigner function, and Boltzmann equation, Phys. Rev. D 37 (1988), 2878–2900.
- [28] C. Carathéodory, Untersuchungen über die Grundlagen der Thermodynamik, Mathematische Annalen 67 (1909), 355–386. A (somewhat inaccurate) English translation, “Investigation into the foundations of thermodynamics”, can be found in pp. 229–256 of: The second law of thermodynamics (J. Kestin, ed.), Dowden, Hutchinson and Ross, Stroudsburg, PA, 1976.
- [29] J. Casas-Vásquez and D. Jou, Temperature in non-equilibrium states: a review of open problems and current proposals, Rep. Prog. Phys. 66 (2003), 1937–2023.
- [30] W.G. Chapman, K.E. Gubbins, G. Jackson and M. Radosz, SAFT: Equation-of-State Solution Model for Associating Fluids. Fluid Phase Equilib. 52 (1989), 31–38.
- [31] W.G. Chapman, K.E. Gubbins, G. Jackson and M. Radosz, New Reference Equation of State for Associating Liquids. Ind. Eng. Chem. Res. 29 (1990), 1709–1721.
- [32] O. Civitarese, P.O. Hess and J.G. Hirsch, Low temperature S-shaped heat capacities in finite nuclei, Rev. Mex. Fís. 50 (2004), 406–411.
- [33] E. Clapeyron, Mémoire sur la puissance motrice de la chaleur. J. l’Ecole Polytechnique 14 (1834), 153–190. Engl. translation pp. 71–105 in: Reflections on the Motive Power of Fire and Other Papers on the Second Law of Thermodynamics (E. Mendoza. ed.), Dover, New York 1960.
- [34] R. Clausius, Über die bewegende Kraft der Wärme und die Gesetze, welche sich daraus fr die Wärmelehre selbst ableiten lassen, Ann. Phys. Chemie 79 (1850), 368–397, 500–524. Engl. translation: On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom, Phil. Mag. 2 (1851), 1–21, 102–119.



- [35] R. Clausius, Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie, Pogg. Ann. 125 (1865), 353–400. English translation pp. 162–193 in: The Second Law of Thermodynamics (J. Kestin, ed.), Dowden, Hutchinson and Ross, Stroudsburg 1976.
- [36] CODATA Internationally recommended values of the Fundamental Physical Constants, Web document (29007).  
<http://physics.nist.gov/cuu/Constants/>
- [37] E.B. Davies, Quantum theory of open systems, Acad. Press, London 1976.
- [38] B.J. Edwards, H.C. Öttinger, R.J.J. Jongschaap, On the relationships between thermodynamic formalisms for complex fluids, J. Non-Equilib. Thermodyn. 23 (1998), 301–333.
- [39] P. Ehrenfest and T. Ehrenfest, Begriffliche Grundlagen der statistischen Auffassung in der Mechanik, Enzykl. Math. Wiss. IV 2.II, Teubner, Leipzig 1911. (Engl. transl: The Conceptual Foundations of the Statistical Approach in Mechanics, Dover Reprints, 2002.)
- [40] R.S. Ellis, An overview of the theory of large deviations and applications to statistical mechanics, Scand. Actuarial J. 1 (1995), 97–142.
- [41] G.G. Emch and C. Liu, The Logic of thermostistical physics, Springer, Berlin 2001.
- [42] G.L. Eyink and H. Spohn, Negative-temperature states and large-scale, long-lived vortices in two-dimensional turbulence, J. Stat. Phys. 70 (1993), 833–886.
- [43] A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen. Cambridge Univ. Press, London 1935.
- [44] D. Forster, Hydrodynamic fluctuations, broken symmetry, and correlation functions, Benjamin, Reading, Mass., 1975.
- [45] R.H. Fowler and E.A. Guggenheim, Statistical thermodynamics Cambridge Univ. Press, Cambridge 1939.
- [46] P. Franklin, Derivatives of higher order as single limits, Bull. Amer. Math. Soc. 41 (1935), 573–582.
- [47] I.M. Gelfand and M.A. Naimark, On the imbedding of normed rings into the ring of operators in Hilbert spaces (in Russian), Mat Sbornik 12 (1943), 197–213.
- [48] J.W. Gibbs, Elementary Principles in Statistical Mechanics. Yale Univ. Press, New Haven 1902. (Reprinted, Dover 1960.)
- [49] V. Gorini, A. Kossakowski, E.C.G. Sudarshan, Completely positive dynamical semi-groups of  $N$ -level systems, J. Math. Phys. 17 (1976), 821–825.

- [50] H. Grabert, Projection Operator Techniques in Nonequilibrium Statistical Mechanics, Springer Tracts in Modern Physics, Berlin 1982.
- [51] H. Grad, The many faces of entropy, *Comm. Pure Appl. Math.* 14 (1961), 323–354.
- [52] W.T. Grandy, Jr., Some issues in thermodynamics, Manuscript, 2001.  
<http://w3.uwyo.edu/~wtg/Issues/IssuesContents.html>
- [53] R.B. Griffiths, A proof that the free energy of a spin system is extensive, *J. Math. Phys* 5 (1964), 1215–1222.
- [54] D.H.E. Gross, Phase Transitions in "Small" Systems – A Challenge for Thermodynamics, *Nucl. Phys. A* 681 (2001), 366–373.
- [55] E. L. Hahn, Spin echoes, *Phys. Rev.* 80 (1950), 580–594.
- [56] E. L. Hahn, Free nuclear induction, *Physics Today* 6 (1953), 4–9.
- [57] H. Haken, *Synergetic: An introduction*. Springer, Berlin 1978.
- [58] S.A. Hassan, A.R. Vasconcellos and R. Luzzi, The informational-statistical-entropy operator in a nonequilibrium ensemble formalism, *Physica A* 262 (1999), 359–375.
- [59] H. Helmholtz, *Über die Erhaltung der Kraft*, Reimer, Berlin 1847.
- [60] D. Home and M.A.B. Whitaker, Ensemble interpretations of quantum mechanics. A modern perspective, *Physics Reports* 210 (1992), 223–317.
- [61] K. Huang, *Statistical Mechanics*. 2nd ed., Wiley, New York 1987.
- [62] E.T. Jaynes, Information Theory and Statistical Mechanics, *Phys. Rev.* 106 (1957), 620–630.
- [63] E.T. Jaynes, Information Theory and Statistical Mechanics II, *Phys. Rev.* 108 (1957), 171–190.
- [64] E.T. Jaynes, *Probability Theory in Science and Engineering*. Socony Mobil Oil Co., Dallas 1958.
- [65] E.T. Jaynes, The Gibbs paradox, pp. 1–22 in: *Maximum Entropy and Bayesian Methods* (C.R. Smith et al., eds.), Kluwer, Dordrecht, 1992
- [66] W.B. Jensen, The Universal Gas Constant R, *Chem. Education Today* 80 (2003), 731–732.
- [67] J.P. Joule, On the calorific effects of magneto-electricity, and on the mechanical value of heat, *Philos. Mag. London* (ser. 4) 23 (1843), 435–443. reprinted in: J.R. Mayer, J. P. Joule, S. Carnot, The discovery of the law of conservation of energy, *Isis* 13 (1929), 18–44.

- [68] N.V. Karlov, Laser-induced chemical reactions, *Applied Optics* 13 (1974), 301–309.
- [69] B.L. Karger, L.R. Snyder and C. Horvath, *An Introduction to Separation Science*, Wiley 1973.
- [70] A. Katz, *Principles of statistical mechanics. The information theory approach*, Freeman, San Francisco 1967.
- [71] A. Kolmogorov, *Foundations of the Theory of Probability*, 2nd English ed., Chelsea, New York 1956.
- [72] K.W. Kratky, Fluctuation of thermodynamic parameters in different ensembles, *Phys. Rev. A* 31 (1985), 945–950.
- [73] R. Kubo, *Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems*, *J. Phys. Soc. Japan* 12 (1957) 570–586.
- [74] R. Kubo, Generalized cumulant expansion method, *J. Phys. Soc. Japan* 17 (1962) 1100–1120.
- [75] T.S. Kuhn, Carnot’s version of “Carnot’s cycle”, *Amer. J. Phys.* 23 (1955), 91–95.
- [76] T.S. Kuhn, La Mer’s version of “Carnot’s cycle”, *Amer. J. Phys.* 23 (1955), 387–389.
- [77] F.L. Lambert, Disorder – a cracked crutch for supporting entropy discussions, *J. Chem. Education* 79 (2002), 187–192.
- [78] L.D. Landau and E.M. Lifshits, *Statistical Physics: Part 1*. 3rd ed., Pergamon Press, Oxford 1980.
- [79] J.L. Lebowitz and H.L. Frisch, Model of Nonequilibrium Ensemble: Knudsen Gas, *Phys. Rev.* 107 (1957), 917–923.
- [80] E.H. Lieb and J. Yngvason, The physics and mathematics of the second law of thermodynamics, *Physics Report* 310 (1999), 1–96.
- [81] G. Lindblad, On the generators of quantum dynamical semigroups, *Commun. Math. Phys.* 48 (1976), 119–130.
- [82] L. Ljung, *System identification: theory for the user*, Prentice-Hall, Upper Saddle River 1986.
- [83] P.C. Martin and J. Schwinger, *Theory of Many-Particle Systems. I* *Phys. Rev.* 115 (1959), 1342–1373.
- [84] A. Aartinez, *An introduction to semiclassical and microlocal analysis*, Springer, New York 2002.

- [85] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York 1996.
- [86] J.R. Mayer, Bemerkungen "uber die Kr"afte der unbelebten Natur, *Ann. Chem. Pharmacie* 42 (1842), 233-240. Engl. translation in: J.R. Mayer, J. P. Joule, S. Carnot, *The discovery of the law of conservation of energy*, *Isis* 13 (1929), 18-44.
- [87] D. Montgomery and G. Joyce, Statistical mechanics of "negative temperature" states, *Phys. Fluids* 17 (1974), 1139-1145.
- [88] H. Mori, Transport, collective motion, and Brownian motion, *Prog Theor Phys* 33 (1965), 423-455.
- [89] R. Mrugala, J. D. Nulton, J. C. Schön, and P. Salamon, Statistical approach to the geometric structure of thermodynamics, *Phys. Rev. A* 41 (1990), 3156-3160.
- [90] I. Müller and T. Ruggeri, *Rational Extended Thermodynamics*, Springer Tracts in Natural Philosophy vol. 37, Springer, New York 1999.
- [91] S.L. Murov, I. Carmichael and G.L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York 1993.
- [92] W. Nernst, Über die Berechnung chemischer Gleichgewichte aus thermischen Messungen, *Nachr. Kgl. Ges. d. Wiss. Göttingen* 6 (1906), 1-40.
- [93] A. Neumaier, Ensembles and experiments in classical and quantum physics, *Int. J. Mod. Phys. B* 17 (2003), 2937-2980. [quant-ph/0303047](https://arxiv.org/abs/quant-ph/0303047)
- [94] A. Neumaier, *The dynamics of thermal states*, in preparation (2007).
- [95] A. Neumaier, *The thermal interpretation of quantum mechanics*, in preparation (2007).
- [96] W. of Ockham, *Philosophical Writings* (P. Boehner, ed.), Nelson, Edinburgh 1957.
- [97] H.C. Oettinger, *Beyond Equilibrium Thermodynamics*, Wiley, Hoboken 2005.
- [98] R.E. Peierls, On a minimum property of the free energy, *Phys. Rev.* 54 (1938), 918-919.
- [99] O. Penrose, Foundations of statistical mechanics, *Rep. Prog. Phys.* 42 (1979), 1937-2006.
- [100] A. Peres, Pure states, mixtures, and compounds, pp. 357-363 in: *Mathematical foundations of quantum theory* (A.R. Maslow, ed.), Acad. Press, New York 1978.
- [101] A. Peres and D.R. Terno, Quantum information and relativity theory, *Rev. Mod. Phys.* 76 (2004), 93-123.
- [102] J. Polonyi and K. Sailer, Renormalization group in internal space, *Phys. Rev. D* 71 (2005), 025010.

- [103] J.M. Prausnitz, R.N. Lichtenthaler and E. Gomes de Azevedo, *Molecular thermodynamics of fluid-phase equilibria*, Prentice Hall, Upper Saddle River 1999.
- [104] E.M. Purcell and R.V. Pound, A nuclear spin system at negative temperature, *Phys. Rev.* 81 (1951), 279–280.
- [105] J. Rau and B. Müller, From reversible quantum microdynamics to irreversible quantum transport, *Physics Rep.* 272 (1996), 1–59.
- [106] L.E. Reichl, *A Modern Course in Statistical Physics*, 2nd. ed., Wiley, New York 1998
- [107] H. Renon and J.M. Prausnitz, Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures, *AIChE J.* 14 (1968), 135–144.
- [108] K. Ridderbos, The coarse-graining approach to statistical mechanics: how blissful is our ignorance? *Studies in History and Philosophy of Modern Physics* 33 (2002), 65–77.
- [109] T.M. Ridderbos and M.L.G. Redhead, The Spin-Echo Experiments and the Second Law of Thermodynamics, *Foundations of Physics* 28 (1998), 1237–1270
- [110] B. Robertson, Equations of motion in nonequilibrium statistical mechanics, *Phys. Rev.* 144 (1966), 151–161.
- [111] R.T. Rockafellar, *Convex Analysis*, Princeton University Press, Princeton 1996.
- [112] R.T. Rockafellar, Second-order convex analysis, *J. Nonlinear Convex Anal.* 1 (1999) 1–16.
- [113] D. Roller, *The early development of the concepts of temperature and heat*, Harvard Univ. Press Cambridge, Mass., 1950.
- [114] J. Rothstein, Nuclear Spin Echo Experiments and the Foundations of Statistical Mechanics, *Amer. J. Physics* 25 (1957), 510–518.
- [115] L. Sklar, *Physics and Chance*, Cambridge Univ. Press, Cambridge 1993.
- [116] F.T. Smith, Diabatic and adiabatic representations for atomic collision problems, *Phys. Rev.* 179 (1969), 111–123.
- [117] H. Spohn, Kinetic equations from Hamiltonian dynamics: Markovian limits, *Rev. Mod. Phys.* 52 (1980), 569–615.
- [118] H.P. Stapp, The Copenhagen interpretation, *Amer. J. Phys.* 40 (1972), 1098–1116.
- [119] W.F. Stinespring, Positive Functions on  $C^*$ -Algebras, *Proc. Amer. Math. Soc.* 6 (1955), 211–216.

- [120] B.N. Taylor, Guide for the Use of the International System of Units (SI), NIST Special Publication 811, 1995 edition.  
<http://physics.nist.gov/cuu/Units/introduction.html>
- [121] D. ter Haar, Foundations of statistical mechanics, *Rev. Mod. Phys.* 27 (1955), 289–338.
- [122] W.E. Thirring, A Course in Mathematical Physics. Vol. 4: Quantum Mechanics of Large Systems. Springer, Berlin 1983.
- [123] W. Thomson, On a universal tendency in nature to the dissipation of mechanical energy, *Phil. Mag.* (4) 4 (1852), 304–306.
- [124] C. Truesdell, The Tragicomical History of Thermodynamics, 1822–1854, Springer, New York 1980.
- [125] C.-Y. Tseng and A. Caticha, Yet another resolution of the Gibbs paradox: an information theory approach, pp. 331–339 in: Bayesian Inference and maximum entropy methods in science and engineering (R.L. Fry, ed.), AIP Conf. Proc. Vol. 617, 2002.
- [126] J. Uffink, Compendium of the foundations of classical statistical physics, *Philosophy of Science Archive*, 2006.  
<http://philsci-archive.pitt.edu/archive/00002691/01/UffinkFinal.pdf>
- [127] D. Wallace, Implications of Quantum Theory in the Foundations of Statistical Mechanics, *Pittsburgh Phil. Sci. Archive*, 2001.  
<http://philsci-archive.pitt.edu/archive/00000410>
- [128] J. Walter, Über G. Falks 'einfachere' Definition des Begriffs der Entropie, *Europ. J. Physics* 7 (1986), 147–147.
- [129] J.A. Wheeler and W.H. Zurek (eds.), *Quantum Theory and Measurements*. Princeton Univ. Press, Princeton 1983.
- [130] P. Whittle, *Probability via expectation*, 3rd ed., Springer, New York 1992.
- [131] G.C. Wick, The Evaluation of the Collision Matrix, *Phys. Rev.* 80 (1950), 268–272.
- [132] C.N. Yang and T.D. Lee, Statistical Theory of Equations of State and Phase Transitions I. Theory of Condensation, *Phys. Rev.* 87 (1952), 404–409.
- [133] D.R. Yarkony, Diabolic conical intersections, *Rev. Mod. Phys.* 68 (1996), 985–1013.
- [134] W.H. Zurek, Decoherence, einselection, and the quantum origins of the classical, *Rev. Mod. Phys.* 75 (2003), 715–775.