Foundations of statistical mechanics for unstable interactions

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Traditional Boltzmann-Gibbs statistical mechanics does not apply to systems with unstable interactions, because for such systems the conventional thermodynamic limit does not exist. In unstable systems the ground state energy does not have an additive lower bound, i.e., no lower bound linearly proportional to the number N of particles or degrees of freedom. In this article unstable systems are studied whose ground state energy is bounded below by a regularly varying function of N with index $\sigma \geqslant 1$. The index $\sigma \geqslant 1$ of regular variation introduces a classification with respect to stability. Stable interactions correspond to $\sigma = 1$. A simple example for an unstable system with $\sigma = 2$ is an ideal gas with a nonvanishing constant two-body potential. The foundations of statistical physics are revisited, and generalized ensembles are introduced for unstable interactions in such a way that the thermodynamic limit exists. The extended ensembles are derived by identifying and postulating three basic properties as extended foundations for statistical mechanics: first, extensivity of thermodynamic systems, second, divisibility of equilibrium states, and third, statistical independence of isolated systems. The traditional Boltzmann-Gibbs postulate, resp. the hypothesis of equal *a priori* probabilities, is identified as a special case of the extended ensembles. Systems with unstable interactions are found to be thermodynamically normal and extensive. The formalism is applied to ideal gases with constant many-body potentials. The results show that, contrary to claims in the literature, stability of the interaction is not a necessary condition for the existence of a thermodynamic limit. As a second example the formalism is applied to the Curie-Weiss-Ising model with strong coupling. This model has index of stability $\sigma = 2$. Its thermodynamic potentials [originally obtained in R. Hilfer, Physica A **320**, 429 (2003)] are confirmed up to a trivial energy shift. The strong coupling model shows a thermodynamic phase transition of order 1 representing a novel mean-field universality class. The disordered high temperature phase collapses into the ground state of the system. The metastable extension of the high temperature free energy to low temperatures ends at absolute zero in a phase transition of order 1/2. Between absolute zero and the critical temperature of the first order transition all fluctuations are absent.

I. INTRODUCTION AND OBJECTIVE

A central *tenet* of equilibrium statistical mechanics holds, that stability of interaction potentials is a *conditio sine qua non* for normal thermodynamic behavior (see, e.g., Refs. [1], p. 378; [2], p. 265; and [3], p. 632). Despite its widespread acceptance this central dogma disagrees with the general practice to assign temperature (i.e., a quantity from normal thermodynamics) to unstable systems such as stars (i.e., to systems outside of normal thermodynamics).

Mathematical models with unstable interactions appear frequently in theoretical physics [4]. A prominent example is given by classical point particles with purely attractive forces (such as gravitation) [5]. It seems less appreciated, that the Curie-Weiss-Ising model without rescaling of the spin-spin coupling strength is a model with unstable interactions [6,7]. One objective in this paper is to provide the derivation of the free energy of the Curie-Weiss-Ising model with unstable interactions (in Ref. [6], p. 430, Eq. (3)) and its entropy (Ref. [7], p. 309, Eq. (4.1)) from first principles. Rigorous discussion of these results is clearly impossible without first revisiting and then extending the foundations of statistical mechanics and thermodynamics. Ensembles for unstable interactions will be introduced in this paper based on fundamental principles, such as extensivity. Model calculations with these extended ensembles are carried out for two examples to demonstrate and exemplify their applicability.

Despite the nonextensivity of unstable systems and the key role played by a certain fractional exponent, called α in this paper, the theory presented here has nothing in common with "nonextensive thermodynamics" [8]. Extensivity remains valid throughout this work and the fractional exponent α in this work is not a free parameter, but determined by the Hamiltonian through Eq. (72) below. In "nonextenstive thermodynamics" [8] extensivity and the zeroth law do not hold, and the fractional exponent q is a free parameter.

Given that stability of interactions and extensivity are fundamental for statistical mechanics, a general theory for unstable interactions necessitates a new perspective on the Boltzmann-Gibbs ensemble hypothesis. Let me emphasize that this modified perspective is implicit, but not explicit, in earlier work [9–18] on the ensemble limit, as witnessed by the results in [6,7]. One can show that the basic formulae (77) and (89) of the present paper are related to Eq. (3.3) in Ref. [15] (p. 68). Rather than to postulate Eqs. (77) and (89) and justify them by their consequences, the objective in this paper is to

obtain these formulae from basic and accepted laws of statistical mechanics. In fact, it will be shown here that the basic principles of equilibrium statistical mechanics follow from three physically natural hypotheses, namely extensivity of the macroscopic energy, divisibility of equilibrium states, and independence of noninteracting systems. Accordingly, these three hypotheses are postulated as three fundamental laws of statistical mechanics. Macroscopic extensivity and existence of thermodynamic potentials are closely related to existence of the thermodynamic limit and stability of interactions [1].

To exhibit the stability problem in an example consider the ideal gas. The Hamilton function for a D-dimensional ideal gas of N point particles of mass m in a region $\mathbb{G} \subset \mathbb{R}^D$ with volume (Lebesgue measure) $V = |\mathbb{G}|$ is generally assumed to be (Refs. [19], p. 46; [20], Eq. (6.42))

$$H_{\mathbb{G}}(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}, \qquad (1)$$

where $\mathbf{r}_i \in \mathbb{G}$ are the positions and $\mathbf{p}_i \in \mathbb{R}^D$ the momenta of the particles. Here it has been assumed that the particles are free in the sense that the potential energy vanishes. In particular, the (two-body) interaction potential $\Phi^{(2)} = 0$ has been assumed to vanish.

Existence of the thermodynamic limit requires that the region $\mathbb{G} = \mathbb{G}(N)$ grows with $N \to \infty$ in such a way that the volume $|\mathbb{G}| = V \to \infty$ diverges and the particle density

$$\rho = \lim_{N \to \infty} \frac{N}{|\mathbb{G}(N)|} \qquad (2)$$

exists in the limit. For finite N the textbook result (Ref. [19], p. 47) for the Helmholtz free energy computed from the canonical ensemble is

$$\mathsf{F}_0(\mathsf{T}, V, N) = -k_B \mathsf{T} \log \left[\frac{V^N (2\pi m k_B \mathsf{T})^{\frac{DN}{2}}}{N! \, h^{DN}} \right], \qquad (3)$$

where T is the temperature of the ideal gas. It is readily seen that the thermodynamic limit exists, and that it yields the thermodynamic potentials of the ideal gas.

The thermodynamic limit does not always exist, if the particles are understood to be free in the sense that they do not exert forces on each other, because a constant nonzero interaction potential $\Phi^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = \Phi_0^{(2)} \neq 0$ is compatible with this understanding. Repeating the computations gives in this case

$$\mathsf{F}(\mathsf{T}, V, N) = \frac{\Phi_0^{(2)}}{2} N(N-1) + \mathsf{F}_0(\mathsf{T}, V, N) \qquad (4)$$

for the free energy. Now, the free energy per particle F/N diverges to $+\infty$ in the limit $N \to \infty$ for $\Phi_0^{(2)} > 0$ and to $-\infty$ for $\Phi_0^{(2)} < 0$. Compared to the case $\Phi_0^{(2)} = 0$ the physical situation is unchanged, because the particles do not exert forces on each other. Especially when $\Phi_0^{(2)} \approx 0$ one would expect the ideal gas laws to remain unchanged. It may come as a surprise to some readers that conventional Boltzmann-Gibbs statistical mechanics does not exist for $\Phi_0^{(2)} \neq 0$, because the thermodynamic limit and hence the thermodynamic potentials do not exist.

As stated in its title the main objective and result of this paper is to introduce a modification of the conventional Boltzmann-Gibbs theory that allows to include unstable interactions into statistical mechanics without violation of extensivity or existence of the thermodynamic limit. Clearly, such an endeavor is tantamount to reestablishing the foundations of Boltzmann-Gibbs statistical mechanics and thermodynamics.

Reestablishing foundations of a physical theory requires to revisit its basic concepts, such as system or state. In thermodynamics the basic concept of a thermodynamic system is described vaguely as some "*piece of the world*" (Ref. [21], p. 17) or as a "*macroscopic system in a static state*" (Ref. [22], p. 6). The basic concept of a thermodynamic variable is vaguely defined as a "*measurable macroscopic quantity which characterizes a system*" (Ref. [23], p. 1). In statistical mechanics the basic concept of an ensemble is usually introduced as a "*collection of identical systems*" (Ref. [20], p. 63) or as "*very many gases at one instant in time*" (Ref. [24], p. 21). Understanding, exploring, or defining the limits of applicability of thermodynamics and statistical mechanics is hardly possible without reformulating these vague ideas more precisely, i.e., more mathematically.

In this paper, ensembles are defined as probability measures on the microscopic phase space, which is 10^{23} dimensional or so. Macroscopic conditions such as constant temperature, pressure, or energy specify submanifolds having practically the same dimensionality (if they are again manifolds), but vanishing volume (Lebesgue measure). This circumstance alone requires a clear and systematic use of probability measures and spaces. This need is exacerbated in the thermodynamic limit in which the phase space becomes infinite dimensional. A brief definition of measure spaces is given in Appendix A.

The thermodynamic limit entails also the necessity to specify domains and their limits mathematically (Refs. [1], Sec. 6, and [25], pp. 13, 46). The vague concept of a thermodynamic system becomes insufficient. Here, a thermodynamic system is defined as a certain type of macroscopic region filled with a substance. More precisely, thermodynamic systems are restricted to finite unions of convex and compact subsets of $\mathbb{R}^3$. The basic definitions are given in Appendix B.

The paper is organized as follows: In Sec. II the importance of extensivity for thermodynamics is discussed. In Sec. III the foundations of statistical mechanics are revisited and reformulated. In the approach introduced here statistical mechanics is based on three fundamental laws formulated in Sec. III E: divisibility of equilibrium states, extensivity of energy, and independence of isolated systems. Section IV formulates classical lattice spins and classical point particles as examples of the approach. It also defines stability of interactions. In Sec. V it is shown that the laws of statistical mechanics formulated in Sec. III E severely restrict the functional form of equilibrium energy distributions. Based on the functional forms of equilibrium energy distributions the generalized equilibrium ensembles are introduced in Sec. VI. The generalized microcanonical ensemble for unstable interactions with instability index $1/\alpha$ is given in Eq. (76) and its partition sum in Eq. (77), while the canonical ensemble and its partition sum are given in Eqs. (88) and (89). These are the main results of this paper. They reduce to the conventional Boltzmann-Gibbs ensembles in the special case $\alpha = 1$.

Finally, in Secs. VII and VIII the generalized ensembles are applied to unstable ideal gases and unstable lattice spin systems. In Sec. VII the new ensembles are applied to the ideal gases with constant K-body interaction. In Sec. VIII the generalized microcanonical and canonical ensembles are applied to the Curie-Weiss-Ising model with strong interactions. Strong interactions means that the coupling constant is not rescaled to zero with the number of spins. In conventional Boltzmann-Gibbs theory the coupling constant is rescaled to ensure existence of the thermodynamic limit (Ref. [26], Eq. (6.52)). The Curie-Weiss-Ising model without rescaling is a textbook example of a system with unstable interactions.

II. FOUNDATIONS OF THERMODYNAMICS

A. Systems and subsystems

Extensivity is fundamental for equilibrium thermodynamics [22,27–29]. Unstable systems are believed to violate extensivity [3]. It is therefore necessary to recall some aspects of the foundations of thermodynamics.

Let $\mathbb{G} \subset \mathbb{R}^D$ denote a subset of $\mathbb{R}^D$, where usually $D = 3$. A *thermodynamic system* is defined to be a region $\mathbb{G}$ filled with a substance (e.g. a fluid). The substance may be a pure substance or a mixture. The amount of substance contained in $\mathbb{G}$ is measured in moles and denoted as $\mathsf{N}(\mathbb{G})$. The mole is a basic unit in the SI system of units. Because arbitrary subsets $\mathbb{G}$ can be very pathological (fractal sets, non-Borel sets, nonmeasurable sets etc.), it is necessary to restrict them. In this paper, the region $\mathbb{G} \subset \mathbb{R}^D$ is defined to be an element of the *convex ring* $\mathscr{R}$, defined as the set of finite unions of convex bodies in Eq. (B1) in Appendix B. Readers who prefer less formal presentations may think of the convex ring as a device to ensure that subsequent statements involving $\mathbb{G}$ do not become invalid due to set-theoretic pathologies.

Two thermodynamic systems $\mathbb{G}_1, \mathbb{G}_2$ are called *isolated from each other* if the interaction between them is negligible. Isolation of a thermodynamic system requires walls. Walls are a basic concept of thermodynamics (Refs. [23], p. 28, and [21], p. 21, footnote 4).

Basic Postulate (Existence of macroscopic walls). *Thermodynamic systems can be isolated experimentally from each other to any desired degree of accuracy by means of (macroscopic) walls.*

A thermodynamic system $\mathbb{G}$ is called *isolated* if the interaction between the substance in $\mathbb{G}$ and substances in the complement $\mathbb{R}^D \setminus \mathbb{G}$ is negligible.

B. States and observables

The *states* of a thermodynamic system can be described by macroscopic thermodynamic quantities (such as volume, energy, entropy, etc.). A macroscopic *thermodynamic quantity* or *observable* A is defined as a continuous, Euclidean invariant functional $\mathsf{A} : \mathscr{R} \to \mathbb{R}$ on the convex ring. Continuity refers to the topology induced by the Hausdorff metric defined in Eq. (B2). A functional A is called *Euclidean invariant* if $\mathsf{A}(g\mathbb{G}) = \mathsf{A}(\mathbb{G})$ holds for all $\mathbb{G} \in \mathscr{R}$ and $g \in \mathbb{R}^D \times SO_D$. Here g is an element from the group $\mathbb{R}^D \times SO_D$ of D-dimensional translations and rotations, and $g\mathbb{G}$ denotes the translated and rotated system $\mathbb{G}$.

Extensive quantities are defined as continuous, Euclidean invariant and additive functionals on $\mathscr{R}$. A given functional $\mathsf{A} : \mathscr{R} \to \mathbb{R}$ is called *additive* if

$$\mathsf{A}(\emptyset) = 0 \tag{5a}$$

$$\mathsf{A}(\mathbb{G}_1 \cup \mathbb{G}_2) = \mathsf{A}(\mathbb{G}_1) + \mathsf{A}(\mathbb{G}_2) - \mathsf{A}(\mathbb{G}_1 \cap \mathbb{G}_2) \tag{5b}$$

holds for all $\mathbb{G}_1, \mathbb{G}_2 \in \mathscr{R}$. Examples of extensive thermodynamic observables are the amount of substance $\mathsf{N}(\mathbb{G})$ or the molar volume. The molar volume $\mathsf{v}(\mathbb{G})$ is defined such that

$$\mathsf{v}(\mathbb{G})\mathsf{N}(\mathbb{G}) = V(\mathbb{G}) = |\mathbb{G}| = \int_{\mathbb{G}} \mathrm{d}^D \mathbf{r} = \int_{\mathbb{R}^D} \chi_{\mathbb{G}}(\mathbf{r}) \mathrm{d}^D \mathbf{r} \tag{6}$$

is the volume where

$$\chi_{\mathbb{G}}(\mathbf{r}) = \begin{cases} 1, & \text{for} \quad \mathbf{r} \in \mathbb{G} \\ 0, & \text{for} \quad \mathbf{r} \notin \mathbb{G} \end{cases} \tag{7}$$

is the indicator function of the set $\mathbb{G} \subset \mathbb{R}^D$.

Thermodynamic equilibrium states are defined as those states, that an <u>isolated</u> thermodynamic system approaches by itself, and that remain invariant under time evolution for a sufficiently long time. Note that equilibrium states may or may not exist for a given system, and that it depends on the system and its evolution how long is "sufficiently long." If there is time scale separation [30], microscopically "long" could be "short" macroscopically. Note also that, although time scales enter at this fundamental level into the definition of thermodynamic equilibrium states, time does not appear explicitly in the mathematical formalism of equilibrium thermodynamics.

C. Laws of thermodynamics

Extensivity is postulated in this paper as a fundamental law of equilibrium thermodynamics. Because of its importance it is proposed to call extensivity the "minus-first law" of thermodynamics. Its formulation is as follows.

Minus-First Law (Extensivity of equilibrium). *Every equilibrium state of a thermodynamic system can be completely characterized by the values of a finite number of extensive quantities.*

Extensivity is important for the thermodynamic limit, i.e., a scaling limit in which $\mathsf{N}(\mathbb{G}) \to \infty$ and $V(\mathbb{G}) \to \infty$ such that the molar volume $\mathsf{v}(\mathbb{G}) = V/\mathsf{N}$ and other molar quantities are constant.

Thermodynamic equilibrium states of a system $\mathbb{G}$ will be denoted as $X(\mathbb{G})$. Let $\mathfrak{A} = \bigcup_{\mathbb{G}} \{X(\mathbb{G})\}$ denote the set of <u>all</u> equilibrium states of <u>all</u> thermodynamic systems. Note that two arbitrary equilibrium states $X_1, X_2 \in \mathfrak{A}$ need not be in equilibrium with each other. The notation $X_1 \overset{\mathfrak{e}}{\sim} X_2$ is introduced to indicate the special case that X_1 is in (complete) equilibrium with X_2. Transitivity of this relation is the zeroth law of thermodynamics.

Zeroth Law (Transitivity of equilibrium). *For any two equilibrium states $X_1, X_2 \in \mathfrak{A}$ there exists an experimental procedure to decide whether $X_1 \overset{\mathfrak{e}}{\sim} X_2$ holds, or not. The relation $X_1 \overset{\mathfrak{e}}{\sim} X_2$ is an equivalence relation for $X_1, X_2 \in \mathfrak{A}$.*

The zeroth law postulates that the set

$$\mathfrak{E} = \{(X_1, X_2) \in \mathfrak{A} \times \mathfrak{A} : X_1 \overset{\mathfrak{e}}{\sim} X_2\} \tag{8}$$

can be determined experimentally (Ref. [31], p. 2), and obeys the properties

$$(X, X) \in \mathfrak{E}, \quad \forall X \in \mathfrak{A} \tag{9a}$$

$$(X_1, X_2) \in \mathfrak{E} \Rightarrow (X_2, X_1) \in \mathfrak{E}, \quad \forall X_1, X_2 \in \mathfrak{A} \tag{9b}$$

$$(X_1, X_2) \in \mathfrak{E} \wedge (X_2, X_3) \in \mathfrak{E} \Rightarrow (X_1, X_3) \in \mathfrak{E},$$
$$\forall X_1, X_2, X_3 \in \mathfrak{A} \tag{9c}$$

characterizing an equivalence relation. In complete (thermal, mechanical, etc.) equilibrium the equivalence classes are isotherms. Any mapping $\Theta : \mathfrak{A} \to \mathbb{R}$, that is constant on isotherms, is called an *empirical temperature*.

The remaining laws of thermodynamics and their consequences are well known and can be found in [21,22,31]. They need not be discussed or repeated here.

III. FOUNDATIONS OF STATISTICAL MECHANICS

A. Systems and subsystems

Statistical mechanical systems are systems composed of a large (ideally infinite) number of microscopic subsystems or degrees of freedom. Kubo [31] (p. 31) writes, "*Systems composed of only a small number of degrees of freedom are not the object of thermodynamics.*" Ruelle emphasizes in point (b) on page 1 of [25], "*The number of subsystems (of a statistical mechanical system) is large*" and on page 1 of [32] even more clearly, "*The formalism of equilibrium statistical mechanics—which we shall call thermodynamic formalism— has been developed since G. W. Gibbs to describe the properties of certain physical systems. These are systems consisting of a large number of subunits (typically 10^{27}) like the molecules of one liter of air or water.*"[1]

Consider a thermodynamic system $\mathbb{G} \in \mathscr{R}$ containing $\mathsf{N}(\mathbb{G})$ moles of a substance with molar volume $\mathsf{v}(\mathbb{G})$. Suppose that it is decomposable as

$$\mathbb{G} = \bigcup_{i=1}^{N} \mathbb{G}_i \tag{10}$$

into a large number $N \gg 1$ of similar or identical *elementary constituents*, *parts*, or *subsystems* $\mathbb{G}_i \in \mathscr{R}$. The decomposition is largely arbitrary. It may even be time dependent. It is subject to the condition that the amount of substance $\mathsf{N}(\mathbb{G}_i)$ in subsystem $\mathbb{G}_i$ obeys

$$\mathsf{N}(\mathbb{G}_i) \approx \mathsf{N}(\mathbb{G}_j) \approx 0 \tag{11}$$

for all pairs $i, j \in \mathfrak{g} = \{1, \dots, N\}$. This *hypothesis of comparable importance* will be formalized in Sec. III E as the *principle of infinite divisibility*. In physical chemistry $\mathsf{N}(\mathbb{G}_i) \approx 1/N_A$ is of the order of the inverse Avogadro constant.

If the subsystems $\mathbb{G}_i$ are chosen such that their mutual overlap volume is small compared to their volume, then

Eq. (11) implies $\mathsf{N}(\mathbb{G}) \approx N\mathsf{N}(\mathbb{G}_i) = N/N_A$ for all i.[2] Homogeneity of the substance requires that the molar volume $\mathsf{v}(\mathbb{G}_i) = \mathsf{v}(\mathbb{G})$ is the same for all i. Equations (10) and (11) imply scale separation. The linear extension of a system is defined as $L(\mathbb{G}) := V(\mathbb{G})^{1/D}$. Then the ratio of microscopic to macroscopic length scales (i.e., the scale separation factor) obeys

$$\frac{L(\mathbb{G})}{L(\mathbb{G}_i)} \approx N^{1/D} \tag{12}$$

for all i. For chemical systems in $D = 3$ with $\mathsf{N}(\mathbb{G}) \approx 10$ one has $N \approx 10^{24}$ and the length scale separation is eight decades, $L(\mathbb{G}) \approx 10^8 L(\mathbb{G}_i)$.

Subsystems correspond to subsets $\mathbb{H} \subset \mathbb{G}$. *Admissible subsystems* are defined as subsets $\mathbb{H} \subset \mathbb{G}$ that obey

$$\frac{V(\mathbb{G}_i \cap \mathbb{H})}{V(\mathbb{G}_i)} \neq \frac{1}{2} \tag{13}$$

for all $i \in \mathfrak{g}$. This condition ensures that every elementary subsystem can be assigned unambiguously. Only admissible subsystems are considered from here on. To each $\mathbb{H} \subset \mathbb{G}$ corresponds a subset $\mathfrak{h} \subset \mathfrak{g}$ of indices defined as

$$\mathfrak{h} = \left\{ i \in \mathfrak{g} : \frac{V(\mathbb{G}_i \cap \mathbb{H})}{V(\mathbb{G}_i)} > \frac{1}{2} \right\}. \tag{14}$$

Two admissible subsystems $\mathbb{H}, \mathbb{H}'$ are called *index equivalent* whenever $\mathfrak{h} = \mathfrak{h}'$. From here on only equivalence classes of index equivalent admissible subsystems will be considered. They will simply be referred to as subsystems.

B. States and observables

The set of states of an elementary subsystem $\mathbb{G}_i$ is denoted as $\Omega(\mathbb{G}_i) = \Omega_i$. It is generally assumed throughout that a field $\mathbb{F}$ of numbers ($\mathbb{F} = \mathbb{R}$ or $\mathbb{F} = \mathbb{C}$) operates on the set of states from the left and from the right; i.e., it is assumed that there exist appropriate maps $\mathbb{F} \times \Omega_i \to \Omega_i$ and $\Omega_i \times \mathbb{F} \to \Omega_i$ compatible with the additive and multiplicative group structure of the number field $\mathbb{F}$.

To cover as many systems as possible (classical, quantum, continuous, discrete, particle, spin, etc.) the set of microstates has to be defined in as general a way as possible. The *state space*, *configuration space*, or *set of microstates* $\Omega_{\mathbb{G}}$, or briefly Ω, of a statistical mechanical system $\mathbb{G}$ is defined as the set of all mappings (see, e.g., Ref. [34], p. 59)

$$\omega_{\mathbb{G}} : \mathfrak{g} \to \bigcup_{i \in \mathfrak{g}} \Omega_i \tag{15}$$

with $\omega_{\mathbb{G}}(i) \in \Omega_i$ for all $i \in \mathfrak{g} = \{1, \dots, N\}$. The notation as a product space

$$\Omega_{\mathbb{G}} = \prod_{i=1}^{N} \Omega_i = \Omega_1 \times \cdots \times \Omega_N \tag{16}$$

will also be used. The *state space of a subsystem* is defined as $\Omega_{\mathbb{H}} = \prod_{i \in \mathfrak{h}} \Omega_i$.

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[1]This view is currently being less emphasized. Contemporary works on the foundations of nonequilibrium statistical mechanics or thermodynamics often consider systems with few degrees of freedom "but still in contact with a heat bath" with many degrees of freedom, that "provides the source of stochastic dynamics" (see, e.g., [33]).

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[2]An exact formula for $\mathsf{N}(\mathbb{G})$ can be derived from Eq. (5), and is given in Eq. (A3) in Appendix A.

The projection $\pi_{\mathbb{H}'}^{\mathbb{H}}$ from a subsystem $\mathbb{H} \subseteq \mathbb{G}$ to a subsystem $\mathbb{H}' \subset \mathbb{H} \subseteq \mathbb{G}$ with nonempty index subset $\mathfrak{h}' \subset \mathfrak{h} \subseteq \mathfrak{g}$ is defined as the mapping

$$\pi_{\mathbb{H}'}^{\mathbb{H}} : \Omega_{\mathbb{H}} \to \Omega_{\mathbb{H}'}$$
$$\omega_{\mathbb{H}} \mapsto \omega_{\mathbb{H}'} = \omega_{\mathbb{H}}|\mathfrak{h}' \qquad (17)$$

that assigns to every map $\omega_{\mathbb{H}}$ in $\Omega_{\mathbb{H}}$ its restriction to the nonempty subset $\mathfrak{h}'$. The abbreviations $\pi_{\mathbb{H}} = \pi_{\mathbb{H}}^{\mathbb{G}}$, $\pi_i^{\mathbb{H}} = \pi_{\mathbb{G}_i}^{\mathbb{H}}$, and $\pi_i = \pi_i^{\mathbb{G}}$ are useful in the following. The projections obey

$$\pi_{\mathbb{H}''}^{\mathbb{H}} = \pi_{\mathbb{H}''}^{\mathbb{H}'} \circ \pi_{\mathbb{H}'}^{\mathbb{H}} \qquad (18)$$

for $\mathfrak{h}'' \subset \mathfrak{h}' \subset \mathfrak{h}$.

The microstates $\omega_{\mathbb{G}_i} \in \Omega_i$ or $\omega_{\mathbb{G}} \in \Omega_{\mathbb{G}}$ are often not directly observable or measurable without uncertainty. A probabilistic framework is needed. It is provided by a σ-algebra $\mathscr{A}_i$ of subsets of Ω_i for each elementary part $\mathbb{G}_i$. For the full system the product σ-algebra

$$\mathscr{A} = \mathscr{A}_{\mathbb{G}} = \bigotimes_{i \in \mathfrak{g}} \mathscr{A}_i = \mathscr{A}_1 \otimes \cdots \otimes \mathscr{A}_N \qquad (19)$$

is defined as the smallest σ-algebra with respect to which all projections π_i are $(\mathscr{A}, \mathscr{A}_i)$-measurable (see [34, p. 60]).

Statistical mechanical states or *mesostates* are probability measures $\mu_{\mathbb{G}}$ on the measurable space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$. This idea seems to go back to Boltzmann [35].

Often a natural *a priori* measure, denoted as $\mu_i = \mu_{\mathbb{G}_i}$, is given on the elementary subsystems $(\Omega_i, \mathscr{A}_i)$. If it is finite, then it becomes an elementary mesostate when normalized. Given such elementary *a priori* measures μ_i, the state space becomes a measure space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, \mu_{\mathbb{G}})$ where

$$\mu_{\mathbb{G}} = \mu_1 \otimes \cdots \otimes \mu_N = \mu_{\mathbb{G}_1} \otimes \cdots \otimes \mu_{\mathbb{G}_N} \qquad (20)$$

is the product measure.

Statistical mechanical observables A are real valued and measurable functions $A : \Omega_{\mathbb{G}} \to \mathbb{R}$. As such they are *random variables* on the probability space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, \mu_{\mathbb{G}})$, once a mesostate $\mu_{\mathbb{G}}$ is given. The most important example is the energy $H_{\mathbb{G}}$ defined below.

The image measure $A(\mu_{\mathbb{G}})$ of $\mu_{\mathbb{G}}$ under the map $A : (\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, \mu_{\mathbb{G}}) \to (\mathbb{R}, \mathscr{B})$ defines the *probability distribution* $W_A(x)$ of the random variable A. Here $\mathscr{B}$ denotes the σ-algebra of Borel-sets in $\mathbb{R}$. Explicitly,

$$W_A(x) = \mu_{\mathbb{G}}\{A \leqslant x\} = \mu_{\mathbb{G}}(\{\omega \in \Omega_{\mathbb{G}} : A(\omega) \leqslant x\}) \qquad (21)$$

is the probability distribution function of random variable A. For $A = H_{\mathbb{G}}$, the probability distribution function $W_{H_{\mathbb{G}}}$ of the energy will be called the *energy distribution in the mesostate* $\mu_{\mathbb{G}}$. The energy distribution is very important, because it permits one to focus attention on the "mesoscopic" probability space $(\mathbb{R}, \mathscr{B}, W_{H_{\mathbb{G}}})$ instead of the more complicated microscopic probability space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, \mu_{\mathbb{G}})$.

Given any set of elementary mesostates μ_i, there exists a family of independent random variables A_i and a probability space such that for every i the probability distribution of A_i is μ_i (Ref. [34], p. 66).

Let $\mathfrak{h} \subset \mathfrak{g} = \{1, \ldots, N\}$ be an index subset corresponding to a subsystem $(\mathbb{H}, \Omega_{\mathbb{H}}, \mathscr{A}_{\mathbb{H}})$. If the system $\mathbb{G}$ is in the mesostate $\mu_{\mathbb{G}}$ then the subsystem $\mathbb{H}$ is in the *projected*

mesostate $\mu_{\mathbb{H}} = \pi_{\mathbb{H}}(\mu_{\mathbb{G}})$. Here $\pi_{\mathbb{H}}(\mu_{\mathbb{G}})$ denotes the image measure of the measure $\mu_{\mathbb{G}}$ under the projection $\pi_{\mathbb{H}}$. Then transitivity of image measures implies for $A : \Omega_{\mathbb{H}} \to \mathbb{R}$

$$W_{A \circ \pi_{\mathbb{H}}}(x) = \mu_{\mathbb{G}}(\{\omega_{\mathbb{G}} \in \Omega_{\mathbb{G}} : A(\pi_{\mathbb{H}}(\omega_{\mathbb{G}})) \leqslant x\})$$
$$= (\pi_{\mathbb{H}}(\mu_{\mathbb{G}}))\{\omega_{\mathbb{H}} \in \Omega_{\mathbb{H}} : A(\omega_{\mathbb{H}}) \leqslant x\}. \qquad (22)$$

The well known transformation formula (Ref. [36], p. 125)

$$\int_{\Omega_{\mathbb{H}}} A(\omega_{\mathbb{H}}) \, d[\pi_{\mathbb{H}}(\mu_{\mathbb{G}})](\omega_{\mathbb{H}}) = \int_{\Omega_{\mathbb{G}}} A(\pi_{\mathbb{H}}(\omega)) \, d\mu_{\mathbb{G}}(\omega) \qquad (23)$$

for integration with respect to an image measure guarantees the consistency condition

$$\langle A \rangle_{\mu_{\mathbb{H}}} = \langle A \rangle_{\pi_{\mathbb{H}} \circ \mu_{\mathbb{G}}} = \langle A \circ \pi_{\mathbb{H}} \rangle_{\mu_{\mathbb{G}}} \qquad (24)$$

for the expectation values of observables $A : \Omega_{\mathbb{H}} \to \mathbb{R}$ of the subsystems. Equation (24) states that the expectation values of subsystem observables A with respect to the projected mesostate $\mu_{\mathbb{H}}$ are the same as those of the "uplifted" observables $A \circ \pi_{\mathbb{H}}$ of the supersystem with respect to $\mu_{\mathbb{G}}$.

The *thermodynamic (macro)states* introduced above are obtained from a mesostate by calculating the expectation values $\langle A_1 \rangle(\mathbb{G}), \ldots, \langle A_k \rangle(\mathbb{G})$ where

$$\langle A_i \rangle(\mathbb{G}) = \int_{\Omega_{\mathbb{G}}} A_i(\omega) d\mu_{\mathbb{G}}(\omega) \qquad (25)$$

with $i = 1, \ldots, k < \infty$. In this way the thermodynamic macrostates are functionals on the convex ring $\mathscr{R}$ in agreement with Sec. II on thermodynamics. Note also that every statistical mechanical observable gives rise to a stochastic process indexed by the sets $\mathbb{G} \in \mathscr{R}$.

C. Microscopic energy

Energy plays a special role and it is an essential part of the definition of a statistical mechanical system. It will be assumed throughout this paper that energy is the only conserved quantity of the underlying microscopic system.

A *statistical mechanical system* with N elementary parts $(\mathbb{G}_i, \Omega_i, \mathscr{A}_i)$, $i = 1, \ldots, N$, is defined as a quadruple $(\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, H_{\mathbb{G}})$ where $\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}$ were defined above, and

$$H_{\mathbb{G}} : \Omega_{\mathbb{G}} \to \overline{\mathbb{R}}$$
$$\omega_{\mathbb{G}} \mapsto H_{\mathbb{G}}(\omega_{\mathbb{G}}; N) \qquad (26)$$

is a measurable function that assigns to every state $\omega_{\mathbb{G}}$ its energy $H_{\mathbb{G}}(\omega_{\mathbb{G}}; N)$. Infinite energies $H_{\mathbb{G}} = \pm\infty$ are allowed.[3]

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[3]For classical systems examples are given in Sec. IV. For quantum systems with N quantum particles the microstate $\omega_{\mathbb{G}}$ is the many-particle wave function subject to the condition that it vanishes whenever one of its arguments is not in $\mathbb{G}$. The set $\Omega_{\mathbb{G}}$ is the many-particle Hilbert space with scalar product $(\cdot, \cdot)$, typically a Sobolev space such as $H^1(\mathbb{R}^{DN})$ for nonrelativistic particles and $H^{1/2}(\mathbb{R}^{DN})$ in the relativistic case. The energy function $H_{\mathbb{G}}$ is specified initially as a quadratic form on $\Omega_{\mathbb{G}}$. If $H_{\mathbb{G}}(\omega_{\mathbb{G}}; N) \geqslant C(\omega_{\mathbb{G}}, \omega_{\mathbb{G}})$ holds for all $\omega_{\mathbb{G}}$, there is a standard method (Ref. [37], p. 177, the Friedrichs extension) of defining the corresponding Hamilton operator $\widehat{H_{\mathbb{G}}}(N)$

Generally, the energy function has the form

$$H_{\mathbb{G}}(\omega_{\mathbb{G}}; N) = H_{\mathbb{G}}(\omega_1, \ldots, \omega_N)$$

$$= \sum_{k=1}^{N} \left(\sum_{\substack{i_1 \in \mathfrak{g} \\ i_1 < \cdots < i_k}} \cdots \sum_{i_k \in \mathfrak{g}} H_{i_1,\ldots,i_k}^{(k)}(\omega_{i_1}, \ldots, \omega_{i_k}) \right) \quad (27)$$

with k-body energies $H_{i_1,\ldots,i_k}^{(k)} : \Omega_{i_1} \times \cdots \times \Omega_{i_k} \to \mathbb{R}$. Here the notation $\omega_{\mathbb{G}_i} = \omega_i$ was used for convenience. Given $H_{\mathbb{G}}$, the energy of a subsystem $\mathbb{H}$ whose elementary parts are labeled by $\mathfrak{h} \subset \mathfrak{g}$ is defined as $H_{\mathbb{H}} : \Omega_{\mathbb{H}} \to \mathbb{R}$ with

$$H_{\mathbb{H}}(\omega_{\mathbb{H}}; |\mathfrak{h}|) = H_{\mathbb{H}}(\pi_{\mathbb{H}}(\omega_{\mathbb{G}}); |\mathfrak{h}|) \quad (28)$$

$$= \sum_{k=1}^{|\mathfrak{h}|} \left(\sum_{\substack{i_1 \in \mathfrak{h} \\ i_1 < \cdots < i_k}} \cdots \sum_{i_k \in \mathfrak{h}} H_{i_1,\ldots,i_k}^{(k)}(\omega_{i_1}, \ldots, \omega_{i_k}) \right),$$

where the functions $H_{i_1,\ldots,i_k}^{(k)} : \Omega_{i_1} \times \cdots \times \Omega_{i_k} \to \mathbb{R}$ are precisely the same as in the definition of $H_{\mathbb{G}}$ [see Eq. (27)]. Here $|\mathfrak{h}|$ is the number of elementary parts of $\mathbb{H}$.

Consider two disjoint subsystems $\mathbb{H}_1, \mathbb{H}_2$ with $\mathbb{H}_1 \cap \mathbb{H}_2 = \emptyset$, labeled by disjoint index sets $\mathfrak{h}_1, \mathfrak{h}_2 \subset \mathfrak{g}$, $\mathfrak{h}_1 \cap \mathfrak{h}_2 = \emptyset$. The union $\mathbb{H} = \mathbb{H}_1 \cup \mathbb{H}_2$ is the compound system composed of the two subsystems. The energy

$$H_{\mathbb{H}_1,\mathbb{H}_2}(\omega_{\mathbb{H}}) = H_{\mathbb{H}_1,\mathbb{H}_2}(\pi_{\mathbb{H}}(\omega_{\mathbb{G}}))$$

$$= H_{\mathbb{H}}(\pi_{\mathbb{H}}(\omega_{\mathbb{G}})) - H_{\mathbb{H}_1}(\pi_{\mathbb{H}_1}(\omega_{\mathbb{G}})) - H_{\mathbb{H}_2}(\pi_{\mathbb{H}_2}(\omega_{\mathbb{G}}))$$

$$= H_{\mathbb{H}}(\omega_{\mathbb{H}}) - H_{\mathbb{H}_1}(\omega_{\mathbb{H}_1}) - H_{\mathbb{H}_2}(\omega_{\mathbb{H}_2}) \quad (29)$$

is called the *interaction energy* between the two subsystems. Two subsystems are called *isolated* if their interaction energy is zero.

D. Stability

The lowest energy, defined as

$$H_{\mathbb{G}}^0(N) = \inf_{\omega_{\mathbb{G}} \in \Omega_{\mathbb{G}}} H_{\mathbb{G}}(\omega_{\mathbb{G}}; N), \quad (30)$$

is called the *ground state energy*. Often there exist states with $H_{\mathbb{G}}(\omega_{\mathbb{G}}; N) = -\infty$. In such cases a regularization procedure is needed. Therefore, the condition

$$H_{\mathbb{G}}^0(N) > -\infty \quad (31)$$

is assumed to hold for all N. The inequality (31) is known as stability of the first kind [38].

Stability of the second kind demands

$$H_{\mathbb{G}}^0(N) \geqslant -BN \quad (32)$$

for all N, where B is a constant independent of N. The second condition of stability excludes, for example, all mathematical models with gravitation [4].

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such that $H_{\mathbb{G}}(\omega_{\mathbb{G}}; N) = (\omega_{\mathbb{G}}, \widehat{H_{\mathbb{G}}}(N)\omega_{\mathbb{G}})$. In the following only classical systems will be discussed.

Equilibrium statistical mechanics is currently restricted to interactions that obey Eq. (32). In this paper interactions that violate (32) will be admitted. Thereby statistical mechanics becomes generalized and applicable to hitherto excluded classes of unstable interactions.

Assuming that the ground state energy $H_{\mathbb{G}}^0(N)$ is a measurable function of N it can be bounded for sufficiently large N by a regularly varying function. To see this, let

$$\sigma^* = \limsup_{N \to \infty} \frac{\log\left[-H_{\mathbb{G}}^0(N)\right]}{\log N} \quad (33)$$

denote the (upper) order of the negative ground state energy (Ref. [39], p. 73). The number

$$\sigma = \max(1, \sigma^*) \quad (34)$$

characterizing the scaling of the ground state behavior of the model will be called its *stability index* (or *index of regular variation*) for the following reason. If it is finite, $\sigma < \infty$, there exists a slowly varying function $\Lambda(N)$ such that

$$H_{\mathbb{G}}^0(N) \geqslant -N^\sigma \Lambda(N) \quad (35)$$

by virtue of Theorem 2.3.11 in Ref. [39] (p. 81). The ground state energy is in general always bounded by a regularly varying function and the special case $\sigma = 1$ and $\Lambda(N) = B$ discussed traditionally corresponds to stability of the second kind [Eq. (32)]. The inequality (35) introduces a classification of stability criteria. It will be called *fractional stability of order* (σ, Λ) or *fractional stability of order* σ whenever Λ is a constant.

Examples for fractional stability of order $\sigma > 1$ occur frequently for mathematical models of real matter. Classical point particles with gravitation have $\sigma = 2$, nonrelativistic bosons with Coulomb interactions have $\sigma = 5/3$, and nonrelativistic bosons or fermions with gravitation have $\sigma = 3$. For more examples see Ref. [4].

E. Laws of statistical mechanics

This section introduces a subclass of mesostates called equilibrium states for macroscopic systems. A system is called *macroscopic* if $L(\mathbb{G})/L(\mathbb{G}_i) \approx N^{1/D} \gg 1$ and if $\mathbb{G}$ can be decomposed into subsystems each of which again contains a macroscopically large number of elementary subsystems.

Equilibrium states are defined as those mesostates that fulfill three fundamental postulates formulated below. These postulates are introduced here as fundamental *laws of statistical mechanics*.

The three laws formalize the experimental fact that it is possible to divide a macroscopic equilibrium system into macroscopic equilibrium subsystems without disturbing thermal equilibrium. This experimental procedure is called *equilibrium preserving insertion or removal of macroscopic constraints or walls*. As an example consider the slow adiabatic insertion of a planar wall into a gas container in a way that does not perturb the pressure and temperature of the gas.

First Law of Statistical Mechanics (Divisibility of equilibrium states). *Consider a macroscopic subsystem* $(\mathbb{H}, \Omega_{\mathbb{H}}, \mathscr{A}_{\mathbb{H}}, H_{\mathbb{H}})$, $\mathbb{H} \subset \mathbb{G}$, *obtained by equilibrium preserving isolation using macroscopic walls from a macroscopic system* $(\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, H_{\mathbb{G}})$. *Here* $H_{\mathbb{H}}$ *is related to* $H_{\mathbb{G}}$ *through Eq. (28)*,

and the interaction energy $H_{\mathbb{H},\mathbb{K}} = 0$, defined in Eq. (29), vanishes for all subsystems $\mathbb{K}$ such that $\mathbb{K} \cap \mathbb{H} = \emptyset$. If $\mu_{\mathbb{G}}$ is an equilibrium state of $(\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, H_{\mathbb{G}})$, then, for every choice of macroscopic wall, the projected mesostate $\mu_{\mathbb{H}} = \pi_{\mathbb{H}}(\mu_{\mathbb{G}})$ is an equilibrium state for the subsystem $(\mathbb{H}, \Omega_{\mathbb{H}}, \mathscr{A}_{\mathbb{H}}, H_{\mathbb{H}})$.

Note that this law excludes Maxwell's demon, because it excludes subsystems defined by microscopic conditions. Microscopic walls are excluded because they would permit the construction of nonequilibrium states from equilibrium states by equilibrium preserving insertion or removal, which would be self-contradictory. (An example would be microscopic walls that separate the subset of particles with velocities in a given interval from the rest.)

Second Law of Statistical Mechanics (Extensivity of energy). *Consider an isolated subsystem as in the first law of statistical mechanics. Then, for every choice of isolating macroscopic wall, there exists a positive number $a > 0$ such that*

$$a\,H_{\mathbb{H}} \stackrel{d}{=} H_{\mathbb{G}} \tag{36}$$

holds; i.e., the equilibrium energy distributions are of the same type.

The notation $X \stackrel{d}{=} Y$ is used for equality in distribution of the two random variables X, Y. It stands for $P_X(x) = P_Y(x)$ at all points of continuity of the two (cumulative) probability distribution functions P_X, P_Y. Thus, Eq. (36) means that $W_{H_{\mathbb{G}}}(E) = W_{H_{\mathbb{H}}}(E/a)$ where

$$W_{H_{\mathbb{G}}}(E) = \mu_{\mathbb{G}}\{\omega_{\mathbb{G}} \in \Omega_{\mathbb{G}} : H_{\mathbb{G}}(\omega_{\mathbb{G}}) \leqslant E\}, \tag{37}$$

$$W_{H_{\mathbb{H}}}(E) = \mu_{\mathbb{G}}\{\omega_{\mathbb{G}} \in \Omega_{\mathbb{G}} : H_{\mathbb{H}}(\pi_{\mathbb{H}}(\omega_{\mathbb{G}})) \leqslant E\}$$
$$= \mu_{\mathbb{H}}\{\omega_{\mathbb{H}} \in \Omega_{\mathbb{H}} : H_{\mathbb{H}}(\omega_{\mathbb{H}}) \leqslant E\} \tag{38}$$

are the equilibrium energy distributions. The mapping $S_F : \mathscr{R} \to \mathbb{R}_+$ assigns to each subsystem $\mathbb{H} \subset \mathbb{G}$ its scale factor from Eq. (36). It will be called the *scale factor functional*.

Basic Postulate (Existence of walls). *The scale factor functional S_F is surjective.*

This assumption plays a similar role as the basic postulate of walls in thermodynamics. Physically this mathematical assumption means that the systems and subsystems have to be macroscopic, so that for every $a > 0$ there exist macroscopic walls that allow to isolate a macroscopic subsystem with scale factor a in Eq. (36).

Third Law of Statistical Mechanics (Independence of isolated systems). *Isolated systems are stochastically independent. In particular, their energies are independent random variables.*

IV. CLASSICAL MODEL SYSTEMS

Before exploring the consequences of the three general laws in Sec. III E it is useful to recall two standard model systems to which the formalism will later be applied.

A. Classical point particles

The most important application of the statistical formalism is classical Newtonian mechanics of point particles. The elementary subsystems $\mathbb{G}_i(t)$ in Newtonian mechanics are called particles and they change with time $t \in \mathbb{R}$. The regions

$\mathbb{G}_i(t) \in \mathscr{R}$ can be chosen arbitrarily subject to the restriction that their volumes are equal:

$$|\mathbb{G}_i| \approx \frac{|\mathbb{G}|}{N} \tag{39}$$

[cf. Eq. (11)]. For point particles one imagines that the mass m_i is concentrated at position $\mathbf{r}_i(t) \in \mathbb{G}_i(t)$. The positions $\mathbf{r}_i(t)$ and momenta $\mathbf{p}_i(t)$ are solutions of Hamilton's equations. If the momenta are denoted with $\mathbf{p}_i(t)$, then $(i = 1, \ldots, N)$

$$\omega_i(t) = (\mathbf{p}_i(t), \mathbf{r}_i(t)), \tag{40a}$$

$$\Omega_i = \mathbb{R}^D \times \mathbb{R}^D = \mathbb{R}^{2D}, \tag{40b}$$

$$\mathscr{A}_i = \mathscr{B}^D \otimes \mathscr{B}^D, \tag{40c}$$

$$\mathrm{d}\mu_i = \prod_{k=1}^{D} \frac{\mathrm{d}p_{ik}}{p_i^{\ominus}} \frac{\mathrm{d}r_{ik}}{r_i^{\ominus}} = \frac{\mathrm{d}\mathbf{p}_i \mathrm{d}\mathbf{r}_i}{h_c^D}, \tag{40d}$$

where $\mathscr{B}^D$ is the Borel σ-algebra in D dimensions. The measure $\mathrm{d}\mu_i$ is the Liouville measure on the one-particle phase space Ω_i nondimensionalized with the units of length $r^{\ominus}$ and momentum $p^{\ominus}$. The dimensional constant defined as

$$h_c = \left(\prod_{i=1}^{N} r_i^{\ominus}\, p_i^{\ominus} \right)^{\frac{1}{N}} \tag{41}$$

has dimensions of action. A general N-body energy function for N classical point particles of mass m_i can be written as

$$
\begin{aligned}
H_{\mathbb{G}}(\omega; N) &= \sum_{k=1}^{N} \left(\sum_{\substack{i_1 \in \mathfrak{g}}} \cdots \sum_{\substack{i_k \in \mathfrak{g} \\ i_1 < \cdots < i_k}} H_{i_1, \ldots, i_k}^{(k)}(\omega_{i_1}, \ldots, \omega_{i_k}) \right) \\
&= H_{\mathbb{G}}(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N) \\
&= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} \Phi^{(1)}(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \Phi^{(2)}(\mathbf{r}_i, \mathbf{r}_j) \\
&\quad + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \sum_{\substack{l=1 \\ l>j}}^{N} \Phi^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_l) + \cdots \\
&\quad + \Phi^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \\
&= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \Phi^{\mathrm{tot}}(\mathbf{r}_1, \ldots, \mathbf{r}_N), \tag{42}
\end{aligned}
$$

where $\Phi^{(k)}(\mathbf{r}_{i_1}, \ldots, \mathbf{r}_{i_k})$ is the hierarchy of k-body potentials. The last equality defines $\Phi^{\mathrm{tot}}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, the total potential energy. The special case with $\Phi^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k) = 0$ for all

$k \geqslant 3$,

$$H_{\mathbb{G}}(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$= \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} \Phi^{(1)}(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \Phi^{(2)}(\mathbf{r}_i, \mathbf{r}_j), \qquad (43)$$

and $\Phi^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = \Phi^{(2)}(\mathbf{r}_i - \mathbf{r}_j)$ is in practice most important. Apparently, many basic interactions in physics are two-body interactions of this type.

B. Classical lattice spin systems

In modern statistical mechanics classical lattice spin systems (and lattice gases) have acquired a central position due to the Heisenberg model [40] and its importance for critical phenomena, solid state physics, and Euclidean field theories [41]. For classical lattice spin systems the elementary subsystems $\mathbb{G}_i$ may be taken as the unit cells of a D-dimensional lattice. The state of each subsystem $\mathbb{G}_i$ is an n-component classical "spin" vector representing, e.g., the order parameter in critical phenomena. One has

$$\omega_i = \left(\omega_i^{(1)}, \ldots, \omega_i^{(n)} \right), \qquad (44)$$

$$\Omega_i = \mathbb{R}^n, \qquad (45)$$

$$\mathscr{A}_i = \mathscr{B}^n, \qquad (46)$$

where $\mathscr{B}^n$ is the Borel σ-algebra in $\mathbb{R}^n$. The *a priori* measure $\mathrm{d}\mu_i$ is defined as a spherically symmetric finite measure

$$\mathrm{d}\mu_i(\omega_i) = g(\omega_i^2)\mathrm{d}\omega_i, \qquad (47)$$

where $\omega_i^2 = \omega_i \cdot \omega_i = \sum \omega_i^{(j)2}$ is the scalar product and $\mathrm{d}\omega_i$ is the Lebesgue measure on $\mathbb{R}^n$. The most important example is the so called φ^4 model given by

$$g(\omega^2) = \exp\left[-\frac{g_4}{4}\omega^4 - \frac{g_2}{2}\omega^2 \right] \qquad (48)$$

with $g_4 \geqslant 0$. It includes many important special cases. The exactly solvable *Gaussian model* is the special case $g_4 = 0$. The *n-vector model* given by

$$g(\omega^2) = \delta(\omega^2 - 1) \qquad (49)$$

is obtained in the limit $g_4 \to \infty$ with $g_2 = -g_4$. Special cases of the n-vector model are the D-dimensional *Ising model* with $n = 1$, the *XY model* with $n = 2$, and the *Heisenberg model* with $n = 3$. The energy function for all these models is usually defined as

$$H_{\mathbb{G}}(\omega) = -\sum_{i=1}^{N} J_i \omega_i - \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} J_{ij} \omega_i \cdot \omega_j, \qquad (50)$$

where $J_i \in \mathbb{R}^n$ and $J_{ij} \geqslant 0$ are one- and two-spin coupling parameters. On a D-dimensional lattice the coupling constants $J_{ij} = 0$ vanish whenever i and j are not nearest neighbors.

V. EQUILIBRIUM ENERGY DISTRIBUTIONS

This section shows that the three basic laws of statistical mechanics introduced above determine the equilibrium energy distributions of statistical mechanical systems up to location and scale factors. The abbreviation

$$\widetilde{H_{\mathbb{G}}} = H_{\mathbb{G}} - H_{\mathbb{G}}^0 \qquad (51)$$

denotes energies shifted by the ground state energy.

A. Stability

Consider two macroscopic subsystems $(\mathbb{H}_i, \Omega_{\mathbb{H}_i}, \mathscr{A}_{\mathbb{H}_i}, H_{\mathbb{H}_i})$ with $i = 1, 2$ both obtained by equilibrium preserving isolation from the same macroscopic system $(\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, H_{\mathbb{G}})$. Let $\mathbb{H}_1 \cup \mathbb{H}_2 = \mathbb{H} \subset \mathbb{G}$. Then $(\mathbb{H}, \Omega_{\mathbb{H}}, \mathscr{A}_{\mathbb{H}}, H_{\mathbb{H}})$ is a third macroscopic subsystem. Its shifted energy function $\widetilde{H_{\mathbb{H}}} = H_{\mathbb{H}} - H_{\mathbb{H}}^0$ is

$$\widetilde{H_{\mathbb{H}}} = \widetilde{H_{\mathbb{H}_1}} + \widetilde{H_{\mathbb{H}_2}} \qquad (52)$$

because $\mathbb{H}_1$ and $\mathbb{H}_2$ are, by construction, isolated from each other, and $H_{\mathbb{H}}^0 = H_{\mathbb{H}_1}^0 + H_{\mathbb{H}_2}^0$. Let the system $\mathbb{G}$ be in some equilibrium state denoted as $\mu_{H_{\mathbb{G}}}$ to indicate its dependence on $H_{\mathbb{G}}$. By the First Law of Statistical Mechanics the image measures are again equilibrium measures. Equation (52) contains three random variables on three different probability spaces. Using the projections $\pi_{\mathbb{H}}, \pi_{\mathbb{H}_i}$ it becomes

$$\widetilde{H_{\mathbb{H}}} \circ \pi_{\mathbb{H}} = \widetilde{H_{\mathbb{H}_1}} \circ \pi_{\mathbb{H}_1} + \widetilde{H_{\mathbb{H}_2}} \circ \pi_{\mathbb{H}_2}, \qquad (53)$$

an equation for random variables on the same probability space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, \mu_{H_{\mathbb{G}}})$.

Let $a_1, a_2 > 0$ be two given positive numbers. Because the scale factor functional S_F is surjective there exist two subsystems $\mathbb{H}_1, \mathbb{H}_2$ isolated by macroscopic walls such that relation (36) holds for each of them. Using (36) and (52) there exists a positive number $a > 0$ such that

$$\frac{1}{a_1}\widetilde{H_{\mathbb{G}}} + \frac{1}{a_2}\widetilde{H_{\mathbb{G}}} \stackrel{d}{=} \widetilde{H_{\mathbb{H}_1}} + \widetilde{H_{\mathbb{H}_2}} = \widetilde{H_{\mathbb{H}}} \stackrel{d}{=} \frac{1}{a}\widetilde{H_{\mathbb{G}}} \qquad (54)$$

holds. In other words, for any two positive numbers $a_1, a_2 > 0$ there exists a third number $a > 0$ such that

$$\frac{1}{a_1}\widetilde{H_{\mathbb{G}}} + \frac{1}{a_2}\widetilde{H_{\mathbb{G}}} \stackrel{d}{=} \frac{1}{a}\widetilde{H_{\mathbb{G}}} \qquad (55a)$$

holds. The systems $\mathbb{H}_1, \mathbb{H}_2$ are isolated and, hence, by the Third Law of Statistical Mechanics the random variables $\widetilde{H_{\mathbb{H}_1}}, \widetilde{H_{\mathbb{H}_2}}$ are independent. Thus, for any $a_1, a_2 > 0$ there exists a constant $a > 0$ such that

$$W_{\widetilde{H_{\mathbb{G}}}}(a_1 E) * W_{\widetilde{H_{\mathbb{G}}}}(a_2 E) = W_{\widetilde{H_{\mathbb{G}}}}(aE) \qquad (55b)$$

holds for the distribution function $W_{\widetilde{H_{\mathbb{G}}}}(E)$ of the random variable $\widetilde{H_{\mathbb{G}}}$. Here $*$ denotes the convolution of distribution functions. A distribution function $W_{\widetilde{H}}$ obeying Eq. (55a) or Eq. (55b) is called *strictly stable* or *stable in the strict sense* [42]. As a consequence of Eqs. (55) the following theorem holds true.

Theorem V.1. *There exists a number α with $0 < \alpha \leqslant 2$ such that the constant a in Eqs. (55) is related through*

$$a = \left(a_1^{-\alpha} + a_2^{-\alpha} \right)^{-1/\alpha} \qquad (56)$$

to the constants a_1, a_2 in Eqs. (55).

The proof follows immediately from Ref. [42] (p. 172, Theorem 3). The number α is called the *characteristic exponent* or *index of stability*.

B. Functional form

Equations (55) determine not only the constant a but also the functional form of $W_{\widetilde{H}_{\mathbb{G}}}$. To see this note that the random variables in Eqs. (55) are all non-negative, because the ground state energy was subtracted. Hence, the distribution $W_{\widetilde{H}_{\mathbb{G}}}(E)$ is concentrated on the interval $[0, \infty]$ and vanishes for $x < 0$. Let

$$w(u) = \left\langle \exp(-u\widetilde{H}_{\mathbb{G}}) \right\rangle = \int_{-\infty}^{\infty} \exp(-uE) \, dW_{\widetilde{H}_{\mathbb{G}}}(E)$$

$$= \int_0^{\infty} \exp(-uE) w(E) \, dE \qquad (57)$$

denote the Laplace-transformed energy distribution, where $w(E) = dW_{\widetilde{H}_{\mathbb{G}}}(E)/dE$ is the density function, if it exists. Laplace transformation of Eq. (55b) gives the functional equation

$$w\left(\frac{u}{a_1}\right) w\left(\frac{u}{a_2}\right) = w\left(\frac{u}{a}\right) \qquad (58)$$

to be satisfied by $w(E)$. Introducing $b_1 = a_1^{\alpha}$ and $b_2 = a_2^{\alpha}$ and using Eq. (56) this becomes

$$w\left(ub_1^{-1/\alpha}\right) w\left(ub_2^{-1/\alpha}\right) = w\left(u(b_1 + b_2)^{-1/\alpha}\right). \qquad (59)$$

Defining the function $f(x) = \log[w(ux^{-1/\alpha})]$ shows that $f(x)$ satisfies the Cauchy functional equation

$$f(x) + f(y) = f(x + y). \qquad (60)$$

The only measurable solution of this equation is the linear map $f(x) = B''x$ with constant B''. From this solution one obtains by inverting the transformations the result

$$w(u) = \exp(B'u^{\alpha}), \qquad (61)$$

where B' is a new constant involving B''. The function $w(u)$ has to be the Laplace transform of a probability distribution, and this restricts its parameters via the following well known theorem (see [42]).

Theorem V.2. *A function $w(u)$ on $[0, \infty]$ is the Laplace transform of a probability distribution $W(E)$ on $[0, \infty]$ if and only if $w(0) = 1$ and it has derivatives of all orders obeying*

$$(-1)^n \frac{d^n w}{du^n} \geqslant 0 \qquad (62)$$

for all n and $u > 0$.

Functions obeying Eq. (62) are called *completely monotone* [42]. The function $w(u)$ in Eq. (61) is completely monotone if and only if $0 < \alpha \leqslant 1$ and $B' \leqslant 0$, as may be verified by calculating its derivatives. Therefore, introducing $B = -B' \geqslant 0$, the Laplace transform of the equilibrium energy distribution has the form

$$w(u) = \exp(-Bu^{\alpha}) = \sum_{k=0}^{\infty} \frac{(-1)^k B^k u^{\alpha k}}{k!}, \qquad (63)$$

where $B \geqslant 0$ and $0 < \alpha \leqslant 1$. Inverting the Laplace transform shows that in the sense of distributions

$$w(E; \alpha, B) = \sum_{k=0}^{\infty} \frac{(-1)^k B^k}{k!} \delta^{(\alpha k)}(E) \qquad (64)$$

holds, where $\delta^{(\alpha)}$ denotes the fractional derivative of order α of the Dirac δ-function [43]. The distribution $\delta^{(\alpha)}(E)$ is defined as $\delta^{(\alpha)}(E) = E^{-\alpha-1}/\Gamma(-\alpha)$ for $E > 0$ and $\delta^{(\alpha)}(E) = 0$ for $E \leqslant 0$. This gives the series expansion

$$w(E; \alpha, B) = \sum_{k=1}^{\infty} \frac{(-1)^k B^k E^{-\alpha k-1}}{\Gamma(k+1)\Gamma(-\alpha k)} \qquad (65)$$

valid for $E > 0$. The important scaling relation

$$w(E; \alpha, B) = B^{-1/\alpha} w(EB^{-1/\alpha}; \alpha, 1) \qquad (66)$$

follows immediately. It shows that the parameter B determines the energy scale and should therefore have dimensions of $[\text{Energy}]^{\alpha}$. The same result can be obtained using Mellin transforms as is shown in Appendix C. The derivation above results in the following theorem.

Theorem V.3. *Consider a macroscopic statistical mechanical system $(\mathbb{G}, \Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}}, H_{\mathbb{G}})$ with stable or fractionally stable energy function $H_{\mathbb{G}}$. If the system is in an equilibrium state $\mu_{H_{\mathbb{G}}}$ then the probability density of shifted energies of the system itself and all its subsystems has the form*

$$w(E; \alpha, B) = \frac{1}{\alpha E} H_{11}^{10}\left(\frac{B^{1/\alpha}}{E} \middle| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix}\right)$$

$$= \sum_{k=1}^{\infty} \frac{(-1)^k B^k E^{-\alpha k-1}}{\Gamma(k+1)\Gamma(-\alpha k)}, \qquad (67)$$

where $0 < \alpha < 1$ and $B \geqslant 0$. This is a one-sided stable density with characteristic exponent α.

To simplify notation the one-sided stable densities of index α will be abbreviated as

$$h_{\alpha}(x) = \frac{1}{\alpha x} H_{11}^{10}\left(\frac{1}{x} \middle| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix}\right)$$

$$= \sum_{k=1}^{\infty} \frac{(-1)^k x^{-\alpha k-1}}{\Gamma(k+1)\Gamma(-\alpha k)} \qquad (68)$$

so that $w(E; \alpha, 1) = h_{\alpha}(E)$ in Eq. (66). Note that this function appears also in the kernel of fractional time evolution operators [12,30,44,45]. The (cumulative) probability distribution is the primitive function

$$H_{\alpha}(x) = \int^x h_{\alpha}(y) dy = \sum_{k=0}^{\infty} \frac{(-1)^k x^{-\alpha k}}{\Gamma(k+1)\Gamma(-\alpha k+1)}. \qquad (69)$$

The characteristic exponent α and the energy scale parameter B are determined by the energy function of the system. This will be seen in the next section.

C. Parameter identification

The previous sections have shown that postulating three general laws of statistical mechanics in Sec. III E implies the functional form for the equilibrium energy distribution given in Eq. (67). Combining Eqs. (21), (67), and (69) gives the scaling law

$$W_{H_{\mathbb{G}}}(E; \alpha, B) = \mu_{\mathbb{G}}(\{\omega \in \Omega_{\mathbb{G}} : H_{\mathbb{G}}(\omega) \leqslant E\})$$

$$= \int_{-\infty}^{E} w(x; \alpha, B) dx = H_{\alpha}\left(\frac{E}{B^{1/\alpha}}\right), \qquad (70)$$

where the value of the two real parameters α, B depends on the Hamilton function $H_{\mathbb{G}}$. These numerical parameters are restricted by the inequalities $0 < \alpha \leqslant 1$ and $B \geqslant 0$. To find the relations $\alpha = \alpha(H_{\mathbb{G}})$ and $B = B(H_{\mathbb{G}})$ of these parameters with $H_{\mathbb{G}}$, observe that the argument $x = E/B^{1/\alpha}$ of $H_\alpha(x)$ in Eq. (70) must be dimensionless so that $B^{1/\alpha} \geqslant 0$ must have dimensions of energy. This suggests to identify the energy $B^{1/\alpha}$ with the suitably shifted and rescaled microscopic energy

$$B^{1/\alpha} \longleftrightarrow a_H\big[H_{\mathbb{G}}(a_\omega\omega) - H_{\mathbb{G}}^0\big] = a_H\widetilde{H_{\mathbb{G}}}(a_\omega\omega) \geqslant 0, \quad (71)$$

where $a_H, a_\omega > 0$ are rescaling factors and $A \longleftrightarrow B$ means that quantity A is to be identified with B. The rescaling factors depend on $N, \alpha,$ and D. Extensivity of energy, understood as linearity in the mole number N, then requires $\sigma\alpha = 1$ or

$$\alpha = \frac{1}{\sigma} \quad (72)$$

as the central result. Equations (70)–(72) provide the fundamental connection between statistical mechanics and the underlying microscopic dynamics governed by $H_{\mathbb{G}}$.

The rescaling $a_\omega\omega$ of the microstates reflects scale separation between microscopic (mechanical) and macroscopic (thermodynamical) descriptions. The thermodynamic limit $N \to \infty$ is a scaling limit. The precise meaning of $a_\omega\omega$ and the choice of rescaling factors depends on the decomposition of the system, on the nature of the microstates, on the underlying mechanics (dynamics), and on the type of scaling limit.

For the purposes of this paper a rescaling of energy is not needed, and $a_H = 1$ is assumed throughout. In general energy rescaling might be unavoidable. The subtraction of $H_{\mathbb{G}}^0$ in Eq. (71) is crucial for the identification. In stable systems the ground state energy is just an additive constant which does not influence the thermodynamic behavior. In the following the dependence of the energy function $H_{\mathbb{G}}$ on the stability parameter α (or σ) will be indicated as $H_{\mathbb{G},\alpha}$ by an additional index when needed.

VI. EQUILIBRIUM ENSEMBLES

A. Equilibrium measure and density of states

The basic result (70) for equilibrium energy distributions on $(\mathbb{R}, \mathscr{B})$ combined with the parameter identifications (71) and (72) suggests the identification of equilibrium measures on $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$. The measure given by H_α on $(\mathbb{R}, \mathscr{B})$ is absolutely continuous with respect to Lebesgue measure and its density function $\mathsf{h}_\alpha(x)$ is non-negative. For fixed N the shift $H_{\mathbb{G},\alpha}^0(N)$ and the rescaling parameters $a_\omega(N)$ are also fixed. These quantities may in general depend also on α, D and other parameters of the system. Combining Eqs. (70), (71), and (69) implies that

$$0 \leqslant \mathsf{H}_\alpha\left(\frac{E}{\widetilde{H_{\mathbb{G},\alpha}}(a_\omega\omega;N)}\right)$$
$$= \int_{-\infty}^{E} \mathsf{h}_\alpha\left(\frac{x}{\widetilde{H_{\mathbb{G},\alpha}}(a_\omega\omega;N)}\right)\frac{\mathrm{d}x}{\widetilde{H_{\mathbb{G},\alpha}}(a_\omega\omega;N)} \leqslant 1 \quad (73)$$

holds true for every microstate $\omega \in \Omega_{\mathbb{G}}$. The integral is the probability that a statistical mechanical system with microscopic energy function $H_{\mathbb{G},\alpha}$ is macroscopically in equi-

librium and has macroscopic energy less than or equal to E, if it is in a given microstate ω. This probability, given by Eq. (73), suggests to use the measure $w(E; \alpha, B)\mathrm{d}E$ in Eq. (70) as guidance to identify the equilibrium measure of a statistical mechanical system with macroscopic energy E. The idea is to replace B in $w(E; \alpha, B)\mathrm{d}E$ with Eq. (71) and $\mathrm{d}E$ with $\mathrm{d}\mu_{\mathbb{G}}(\omega)$ to obtain $w(E; \alpha, H_\alpha(\omega))\mathrm{d}\mu_{\mathbb{G}}(\omega)$. This then suggests to <u>define</u> the equilibrium measure $\mu_{H_{\mathbb{G},\alpha}}(\,\cdot\,; E, \mathbb{G}, N)$ of a statistical mechanical system $\mathbb{G}$ with microscopic energy function $H_{\mathbb{G},\alpha}$, macroscopic energy E, volume $V = |\mathbb{G}|$, and number of subsystems N on the measurable space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$ of microstates by

$$\mu_{H_{\mathbb{G},\alpha}}(X; E, \mathbb{G}, N) = \int_X \frac{1}{H_\alpha(\omega)}\mathsf{h}_\alpha\left[\frac{E}{H_\alpha(\omega)}\right]\mathrm{d}\mu_{\mathbb{G}}(\omega) \quad (74)$$

for all sets $X \in \mathscr{A}_{\mathbb{G}}$, where the abbreviated notation[4]

$$H_\alpha(\omega) = \widetilde{H_{\mathbb{G},\alpha}}(a_\omega\omega; N)$$
$$= H_{\mathbb{G},\alpha}[a_\omega(N)\omega; N] - H_{\mathbb{G},\alpha}^0(N) \quad (75)$$

has been used. Equation (74) defines a measure on $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$, because the integrand is a non-negative measurable function (Ref. [36], p. 109). In general, the given *a priori* measure $\mu_{\mathbb{G}}$ does not have to be a probability measure, but is here always assumed to be a σ-finite measure. Then the Radon-Nikodym theorem implies that the equilibrium measure $\mu_{H_{\mathbb{G}}}$ is absolutely continuous with respect to the *a priori* measure $\mu_{\mathbb{G}}$ (Ref. [36], p. 116). For $X = \Omega_{\mathbb{G}}$ the measure of the full space $\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N)$ is the *density of states*.

B. Microcanonical ensemble

For $\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N) < \infty$ the *generalized microcanonical ensemble* (or *generalized microcanonical mesostate*) for stable ($\alpha = 1$) as well as unstable ($0 < \alpha < 1$) systems is defined as the probability measure

$$\rho_{\mathsf{S}}(X; E, \mathbb{G}, N; H_{\mathbb{G},\alpha}) = \frac{\mu_{H_{\mathbb{G},\alpha}}(X; E, \mathbb{G}, N)}{\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N)} \quad (76)$$

for all $X \in \mathscr{A}_{\mathbb{G}}$ on the measurable space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$ of microscopic states. It gives the probability to find the system $\mathbb{G}$ in equilibrium in a microstate $\omega \in X \subset \Omega_{\mathbb{G}}$ with energy E. The *generalized microcanonical partition sum* is defined as the (indefinite) integral (primitive function)

$$Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G},\alpha}) = \int \mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N)\,\mathrm{d}E \quad (77)$$
$$= \iint_{\Omega_{\mathbb{G}}} \frac{1}{H_\alpha(\omega)}\mathsf{h}_\alpha\left[\frac{E}{H_\alpha(\omega)}\right]\mathrm{d}\mu_{\mathbb{G}}(\omega)\mathrm{d}E$$

of the density of states, so that

$$\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N) = \frac{\mathrm{d}}{\mathrm{d}E}Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G},\alpha}) \quad (78)$$

holds. This allows to calculate microcanonical expectation values as

$$\langle A(\omega)\rangle_\alpha = \Delta E \frac{\partial}{\partial E}\int_{\Omega_{\mathbb{G}}} A(\omega)\mathrm{d}\rho_{\mathsf{S}}(\omega; E, \mathbb{G}, N; H_{\mathbb{G},\alpha}), \quad (79)$$

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[4]Note that H_α in Eq. (75) differs from H_α in Eqs. (69) and (73).

where ΔE is the thickness of the energy shell. Under appropriate conditions this yields the extended equipartition law

$$\left\langle \omega_i \frac{\partial H_{\mathbb{G}}(\omega)}{\partial \omega_j} \right\rangle_\alpha = \delta_{ij} \left\{ \frac{\mathrm{d}}{\mathrm{d}E} \log \left[Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G},\alpha}) \right] \right\}^{-1} \quad (80)$$

of energy, provided the generalized virial is well defined.

The argument $\mathbb{G}$ in the function Z_{S} stands for the dependence on volume $V = |\mathbb{G}|$ and other macroscopic geometric parameters. The dependence on $H_{\mathbb{G}}$ stands for extensive parameters appearing in the Hamilton function. For general systems other parameters such as electric and magnetic polarizations, displacements, etc., might appear in the microscopic energy function.

For $\alpha \to 1$ Eq. (63) gives $\mathrm{h}_1(x) = \delta(x-1)$ and the result in Eq. (70) becomes

$$Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G}})$$
$$= \int_{\Omega_{\mathbb{G}}} \delta \left(E - H_{\mathbb{G}}(a_\omega \omega) + H_{\mathbb{G}}^0 \right) \mathrm{d}\mu_{\mathbb{G}}(\omega) \quad (81)$$

for systems with stable interactions ($\alpha = 1$). Except for a factor $N!$ Eq. (81) resembles the usual microcanonical ensemble

$$Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G}}) = \frac{1}{N!} \int_{\Omega_{\mathbb{G}}} \delta(E - H_{\mathbb{G}}(\omega)) \, \mathrm{d}\mu_{\mathbb{G}}(\omega) \quad (82)$$

if $a_\omega = 1$, which is generally accepted for $\alpha = 1$.

Most authors [19,20,27,46,47] assume extensivity (i.e., the Minus-First Law) for entropy itself (instead of for entropy differences as stressed in [48]) and postulate $\mathsf{S} = k_B \log Z_{\mathsf{S}}$ for finite systems. In this work the connection between statistical mechanics and equilibrium thermodynamics is formulated as

$$\mathsf{u} = N_A \lim_{E,N \to \infty} \frac{E}{N}, \quad (83a)$$

$$\mathsf{s}(\mathsf{u}, \mathsf{v}; \alpha) = k_B N_A \lim_{E, |\mathbb{G}|, N \to \infty} \frac{\log Z_{\mathsf{S}}(E, \mathbb{G}, N; H_{\mathbb{G},\alpha})}{N}, \quad (83b)$$

in the thermodynamic limit $E, |\mathbb{G}|, N \to \infty$ with finite E/N, $|\mathbb{G}|/N$ and suitable restrictions on the shape of $\mathbb{G}$. Here s is molar entropy, u is molar internal energy, and v is molar volume. Equations (83) hold for all $0 < \alpha \leqslant 1$, the case $\alpha = 1$ covering stable interactions. The thermodynamic limit is needed, if one wants the different ensembles to yield the same result.

C. Canonical ensemble

The microcanonical ensemble applies to isolated systems, the canonical ensemble to systems $\mathbb{G}$ in contact with a heat reservoir $\mathbb{G}_{\mathsf{T}}$ at reservoir temperature T. Treating the combined system $\mathbb{G} \cup \mathbb{G}_{\mathsf{T}}$ microcanonically with Hamilton function $H_{\mathbb{G} \cup \mathbb{G}_{T},\alpha}$ the energy $H_{\mathbb{G},\alpha}$ of the (now sub)system $\mathbb{G}$ becomes a random variable. Integration over all states $\Omega_{\mathbb{G}_{\mathsf{T}}}$ of the reservoir or Laplace transformation of Eq. (74) yields

$$\mu_{H_{\mathbb{G},\alpha}}(X; \mathsf{T}, \mathbb{G}, N) = \int_0^\infty e^{-\beta E} \mu_{H_{\mathbb{G},\alpha}}(X; E, \mathbb{G}, N) \, \mathrm{d}E, \quad (84)$$

$$\beta = \frac{1}{k_B \mathsf{T}} \quad (85)$$

for every set $X \in \mathscr{A}_{\mathbb{G}}$. To evaluate Eq. (84) in applications the formula

$$\int_0^\infty e^{-ux} \mathrm{h}_\alpha(x) \mathrm{d}x = \int_0^\infty e^{-ux} \frac{1}{\alpha x} \mathrm{H}_{11}^{10} \left(\frac{1}{x} \bigg| \begin{matrix} (0,1) \\ (0, 1/\alpha) \end{matrix} \right) \mathrm{d}x$$
$$= \exp(-u^\alpha) \quad (86)$$

is useful. It is readily obtained either from Eq. (61) or from the series expansions. Inserting Eq. (74) into Eq. (84) and using this formula gives

$$\mu_{H_{\mathbb{G},\alpha}}(X; \mathsf{T}, \mathbb{G}, N) = \int_X \exp \left\{ -[\beta H_\alpha(\omega)]^\alpha \right\} \mathrm{d}\mu_{\mathbb{G}}(\omega) \quad (87)$$

for all sets $X \in \mathscr{A}_{\mathbb{G}}$. The *generalized canonical ensemble* (or *generalized canonical mesostate*) for stable ($\alpha = 1$) as well as unstable ($0 < \alpha < 1$) systems is defined as the probability measure

$$\rho_{\mathsf{F}}(X; \mathsf{T}, \mathbb{G}, N; H_{\mathbb{G},\alpha}) = \frac{\mu_{H_{\mathbb{G},\alpha}}(X; \mathsf{T}, \mathbb{G}, N)}{\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; \mathsf{T}, \mathbb{G}, N)} \quad (88)$$

for all $X \in \mathscr{A}_{\mathbb{G}}$ on the measurable space $(\Omega_{\mathbb{G}}, \mathscr{A}_{\mathbb{G}})$ of microscopic states. The normalization factor

$$Z_{\mathsf{F}}(\mathsf{T}, \mathbb{G}, N; H_{\mathbb{G},\alpha}) = \mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; \mathsf{T}, \mathbb{G}, N) \quad (89)$$

$$= \int_{\Omega_{\mathbb{G}}} \exp[-(\beta \widetilde{H_{\mathbb{G},\alpha}}(a_\omega \omega))^\alpha] \mathrm{d}\mu_{\mathbb{G}}(\omega)$$

is the *generalized canonical partition sum*. For stable interactions with $\alpha = 1$ and $a_\omega = 1$ this becomes

$$Z_{\mathsf{F}}(\mathsf{T}, \mathbb{G}, N; H_{\mathbb{G}}) = \int_{\Omega_{\mathbb{G}}} \exp[-\beta \widetilde{H_{\mathbb{G}}}(\omega)] \mathrm{d}\mu_{\mathbb{G}}(\omega), \quad (90)$$

the canonical Boltzmann-Gibbs measure apart from a prefactor due to the energy shift. The connection with thermodynamics is now given as

$$\mathsf{f}(\mathsf{T}, \mathsf{v}; \alpha) = -k_B N_A \mathsf{T} \lim_{|\mathbb{G}|, N \to \infty} \frac{\log Z_{\mathsf{F}}(\mathsf{T}, \mathbb{G}, N; H_{\mathbb{G},\alpha})}{N} \quad (91)$$

in the thermodynamic limit $|\mathbb{G}|, N \to \infty$ with $|\mathbb{G}|/N$ fixed and suitable restrictions on the shape of $\mathbb{G}$. Here f is the molar Helmholtz free energy and v is the molar volume.

D. Grandcanonical ensemble

Grandcanonically the system $\mathbb{G}$ is coupled to a heat reservoir $\mathbb{G}_{\mathsf{T}}$ at temperature T and an N-reservoir $\mathbb{G}_\mu$ at chemical potential μ. The combined system $\mathbb{G} \cup \mathbb{G}_{\mathsf{T}} \cup \mathbb{G}_\mu$ is discussed in the canonical ensemble. The grandcanonical partition sum becomes

$$Z_{\Xi}(\mathsf{T}, \mathbb{G}, \mu; H_{\mathbb{G},\alpha}) = \sum_{N=1}^\infty e^{\beta \mu N} Z_{\mathsf{F}}(\mathsf{T}, \mathbb{G}, N; H_{\mathbb{G},\alpha}) \quad (92)$$

and the thermodynamic limit has to be taken as an infinite volume limit $|\mathbb{G}| \to \infty$. With suitable restrictions on $\mathbb{G}$ it yields the pressure

$$\mathsf{p}(\mathsf{T}, \mu; \alpha) = k_B \mathsf{T} \lim_{|\mathbb{G}| \to \infty} \frac{\log Z_{\Xi}(\mathsf{T}, \mathbb{G}, \mu; H_{\mathbb{G},\alpha})}{|\mathbb{G}|} \quad (93)$$

as function of temperature T and chemical potential μ.

E. T-p ensemble

In the T-p ensemble the system is coupled to a volume reservoir. The partition function of the T-p ensemble is computed as the Laplace transform with respect to volume $V = |\mathbb{G}|$

$$Z_G(\mathsf{T}, \mathsf{p}, N; H_{\mathbb{G},\alpha}) = \int_0^\infty e^{-\beta \mathsf{p}|\mathbb{G}|} Z_F(\mathsf{T}, |\mathbb{G}|, N; H_{\mathbb{G},\alpha}) \mathrm{d}|\mathbb{G}| \tag{94}$$

of the canonical partition function. The molar Gibbs potential

$$g(\mathsf{T}, \mathsf{p}; \alpha) = -k_B N_A \mathsf{T} \lim_{N \to \infty} \frac{\log Z_G(\mathsf{T}, \mathsf{p}, N; H_{\mathbb{G},\alpha})}{N} \tag{95}$$

is then obtained in the thermodynamic limit.

VII. APPLICATION TO IDEAL GASES

Ideal gases and their thermodynamic limit are fundamental for statistical mechanics, because heat reservoirs are infinite ideal gases. The relationship between statistical mechanics and thermodynamics given in Eqs. (83) or (91) is usually established for the Hamilton function of the ideal gas, and then extrapolated to other cases.

A. Microscopic states and energies

In thermodynamics the monatomic ideal gas is defined by the ideal gas laws

$$\mathsf{pv} = k_B N_A \mathsf{T}, \tag{96a}$$

$$\mathsf{u} = \tfrac{3}{2} k_B N_A \mathsf{T}, \tag{96b}$$

where p is pressure, v is molar volume, T is temperature, N_A is Avogadro's constant, and k_B is Boltzmann's constant.

In statistical mechanics the ideal gas is defined as a system of $N \gg 1$ noninteracting point particles (subsystems). It is fundamental to derive the ideal gas laws from this model. Point particles are called noninteracting when there are no forces between them. Noninteracting does not imply that all potential energies vanish, but only that potential gradients vanish. The generalized ideal gas models are defined by

$$\Phi^{(k)}(\mathbf{r}_{i_1}, \dots, \mathbf{r}_{i_k}) = \frac{\Phi_0^{(k)}}{\chi_\mathbb{G}(\mathbf{r}_{i_1}) \cdots \chi_\mathbb{G}(\mathbf{r}_{i_k})} \tag{97}$$

in Eq. (42), where $\Phi_0^{(k)}$, $k = 1, \dots, N$ are constants. The indicator function $\chi_\mathbb{G}(\mathbf{r})$ of the set $\mathbb{G} \subset \mathbb{R}^D$ restricts the particles to the region $\mathbb{G}$ by means of an infinite potential energy penalty.

For simplicity only the special case where $\Phi_0^{(k)} = 0$ for all k except $k = K$ with $K \leqslant [N/2]$ is considered. Here $[x]$ denotes the largest integer smaller than x. The choice $\Phi_0^{(k)} = 0$ for $0 \leqslant k < K$ is made, mainly because it simplifies subsequent expressions. The final result remains unchanged in the more general case. The energy function of K-body ideal gases

is then the sum of the total kinetic and potential energy

$$H_{\mathbb{G},K}(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \Phi^{\mathrm{tot}}(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$$\Phi^{\mathrm{tot}} = \sum_{i_1=1}^N \sum_{\substack{i_2=1 \\ i_2 > i_1}}^N \cdots \sum_{\substack{i_K=1 \\ i_K > i_{K-1}}}^N \frac{\Phi_0^{(K)}}{\chi_\mathbb{G}(\mathbf{r}_{i_1}) \cdots \chi_\mathbb{G}(\mathbf{r}_{i_K})} \tag{98}$$

and reduces to the standard ideal gas for $\Phi_0^{(K)} = 0$. It defines a system of particles that do not exert forces on each other.

The ground state has $\mathbf{p}_i = 0$ and $\mathbf{r}_i \in \mathbb{G}$ for all i. The ground state energy

$$H_{\mathbb{G},K}^0 \overset{(30)}{=} \binom{N}{K} \Phi_0^{(K)}$$

$$= \frac{\Phi_0^{(K)}}{K!} N(N-1)(N-2) \cdots (N-K+1) \tag{99}$$

implies $\sigma = K$ from Eq. (34).

B. Rescaling factors

To compute the partition sums a rescaling of states as in Eq. (71) is needed for correct Boltzmann counting and extensivity in the thermodynamic limit. The rescaling of positions and momenta with the number N of elementary parts reflects separation of scales (change of resolution) between the underlying microscopic system and the macroscopic thermodynamic system. If $\Phi_0^{(K)} < 0$ is negative, then the potential energy diverges as $\sim -N^\sigma$ to $-\infty$ in the limit $N \to \infty$. If the total energy is fixed, this implies that the kinetic energy diverges as $\sim N^\sigma$, and hence the velocities $|\mathbf{v}_i|$ scale as $\sim N^x$ with $x = (\sigma - 1)/2$. The state rescaling in Eq. (71) is

$$a_\omega \omega_i = (a_p \mathbf{p}_i, a_r \mathbf{r}_i) \tag{100}$$

with $a_\omega = a_\omega(N, \alpha, D)$, where the rescaling factors for position a_r and momentum a_p are chosen as

$$a_r = [\Gamma(N+1)]^{\frac{1}{DN}} \sim N^{\frac{1}{D}}, \tag{101a}$$

$$a_p = \left[\frac{\Gamma\left(\frac{DN}{2\alpha} + 1\right)}{\Gamma\left(\frac{DN}{2} + 1\right)} \right]^{\frac{1}{DN}} \sim N^{\frac{(\sigma-1)}{2}}. \tag{101b}$$

The rescaling of position ensures correct Boltzmann counting, while the rescaling of momentum ensures existence of the thermodynamic limit.

C. Microcanonical partition sum

The microcanonical partition sum in Eq. (77), or the density of states $\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}}; E, \mathbb{G}, N)$, for the generalized ideal gas models defined in Eq. (98) have to be computed from ensembles with stability index $\alpha = 1/K$ with $K \in \mathbb{N}$. Inserting

Eq. (98) gives

$$\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}};E,\mathbb{G},N) = \int_{\Omega_{\mathbb{G}}} \frac{1}{\left[H_{\mathbb{G},K}(a_\omega\omega)-H_{\mathbb{G}}^0\right]}\mathrm{h}_\alpha\left(\frac{E}{\left[H_{\mathbb{G},K}(a_\omega\omega)-H_{\mathbb{G}}^0\right]}\right)\mathrm{d}\mu_{\mathbb{G}}(\omega)$$

$$= \int_{\mathbb{R}^D}\cdots\int_{\mathbb{R}^D}\frac{1}{H_{\mathbb{G},K}(a_p\mathbf{p}_1,\ldots,a_r\mathbf{r}_N)-H_{\mathbb{G}}^0}\mathrm{h}_{1/K}\left(\frac{E}{H_{\mathbb{G},K}(a_p\mathbf{p}_1,\ldots,a_r\mathbf{r}_N)-H_{\mathbb{G}}^0}\right)\frac{\mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{p}_N\mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_N}{h_c^{DN}}$$

$$= \prod_{i=1}^N (2m_i)^{D/2}\int_{\mathbb{R}^D}\cdots\int_{\mathbb{R}^D}\frac{1}{H_{\mathbb{G},K}(\mathbf{p}_1,\ldots,\mathbf{r}_N)-H_{\mathbb{G}}^0}\mathrm{h}_{1/K}\left(\frac{E}{H_{\mathbb{G},K}(\mathbf{p}_1,\ldots,\mathbf{r}_N)-H_{\mathbb{G}}^0}\right)\frac{\mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{r}_N}{(a_pa_rh_c)^{DN}}$$

$$= \frac{|\mathbb{G}|^N M_N}{(a_pa_rh_c)^{DN}}\int_{\mathbb{R}^D}\cdots\int_{\mathbb{R}^D}\frac{1}{\sum_1^N \mathbf{p}_i^2}\mathrm{h}_{1/K}\left(\frac{E}{\sum_1^N \mathbf{p}_i^2}\right)\mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{p}_N, \tag{102}$$

where Eqs. (72), (100), and (99) were used. In the last equality the integrations over all $\mathbf{r}_i$ were performed by noting that $\mathrm{h}_{1/K}(0)=0$ and $H_{\mathbb{G}}(\mathbf{p}_1,\ldots,\mathbf{r}_N)=\infty$ for any $\mathbf{r}_i\notin\mathbb{G}$. With $M_N=\prod_{i=1}^N(2m_i)^{D/2}$ and Eq. (68) the integrations over $\mathbf{p}_i$ become

$$\mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}};E,\mathbb{G},N) = \frac{K|\mathbb{G}|^N M_N}{(a_pa_rh_c)^{DN}}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\frac{1}{E}\mathrm{H}_{11}^{10}\left(\frac{\sum_{j=1}^{DN}x_j^2}{E}\bigg|{(0,1)\atop(0,K)}\right)\mathrm{d}x_1\cdots\mathrm{d}x_{DN}$$

$$\overset{(\mathrm{F2})}{=} \frac{K|\mathbb{G}|^N M_N}{E(a_pa_rh_c)^{DN}}\frac{DN\pi^{DN/2}}{\Gamma\left(\frac{DN}{2}+1\right)}\int_0^\infty \mathrm{H}_{11}^{10}\left(\frac{y^2}{E}\bigg|{(0,1)\atop(0,K)}\right)y^{DN-1}\mathrm{d}y$$

$$= \frac{|\mathbb{G}|^N M_N}{E(a_pa_rh_c)^{DN}}\frac{KDN\pi^{DN/2}}{2\Gamma\left(\frac{DN}{2}+1\right)}\int_0^\infty \mathrm{H}_{11}^{10}\left(\frac{y}{E}\bigg|{(0,1)\atop(0,K)}\right)y^{(DN/2)-1}\mathrm{d}y$$

$$\overset{(\mathrm{F3})}{=} \frac{|\mathbb{G}|^N M_N}{E(a_pa_rh_c)^{DN}}\frac{KDN(\pi E)^{DN/2}}{2\Gamma\left(\frac{DN}{2}+1\right)}\frac{\Gamma\left(\frac{KDN}{2}\right)}{\Gamma\left(\frac{DN}{2}\right)}$$

$$= \prod_{i=1}^N \sqrt{m_i^D}\frac{|\mathbb{G}|^N(2\pi E)^{DN/2}}{(h_ca_pa_r)^{DN}}\frac{\Gamma\left(\frac{DN}{2\alpha}+1\right)}{\Gamma\left(\frac{DN}{2}+1\right)\Gamma\left(\frac{DN}{2}\right)}\frac{1}{E}, \tag{103}$$

where $|\mathbb{G}|=V(\mathbb{G})$ is the volume of $\mathbb{G}$. Here Eqs. (F2) and (F3) have been used as indicated. The abbreviation M_N was resubstituted in the last step. For a monatomic ideal gas with $m_i=m$ the exact final result is obtained by integration with respect to E as

$$Z_\mathsf{S}(E,\mathbb{G},N;H_{\mathbb{G},\alpha}) = \int \mu_{H_{\mathbb{G},\alpha}}(\Omega_{\mathbb{G}};E,\mathbb{G},N)\,\mathrm{d}E = \frac{|\mathbb{G}|^N}{(a_ra_ph_c)^{DN}}\frac{(2\pi mE)^{DN/2}}{\Gamma\left(\frac{DN}{2}+1\right)}\frac{\Gamma\left(\frac{DN}{2\alpha}+1\right)}{\Gamma\left(\frac{DN}{2}+1\right)}. \tag{104}$$

Inserting the rescaling factors from Eq. (101) and identifying $h_c=h$ with Planck's constant reproduces the ideal gas result

$$Z_\mathsf{S}(E,\mathbb{G},N;H_{\mathbb{G},\alpha}) = \frac{|\mathbb{G}|^N}{h^{DN}N!}\frac{(2\pi mE)^{DN/2}}{\Gamma\left(\frac{DN}{2}+1\right)} \tag{105}$$

independent of the index of stability $\alpha=1/K$ for all $K\in\mathbb{N}$. Inserting the result Z_S into Eq. (83) gives the molar entropy of the ideal gas [19] and by differentiation the ideal gas laws (96).

D. Canonical partition sum

The canonical partition function is computed from Eq. (89) with $\alpha=1/K$ as

$$Z_\mathsf{F}(\mathsf{T},\mathbb{G},N;H_{\mathbb{G},1/\alpha}) = \int_{\mathbb{R}^D}\cdots\int_{\mathbb{R}^D}\exp\left\{-\left[\beta\left(H_{\mathbb{G},1/\alpha}(a_p\mathbf{p}_1,\ldots,a_r\mathbf{r}_N)-H_{\mathbb{G},1/\alpha}^0\right)\right]^\alpha\right\}\frac{\mathrm{d}\mathbf{p}_1\cdots d\mathbf{r}_N}{h_c^{DN}}$$

$$= \frac{|\mathbb{G}|^N}{(a_ra_ph_c)^{DN}}\int_{\mathbb{R}^D}\cdots\int_{\mathbb{R}^D}\exp\left\{-\left[\frac{\beta}{2m}\sum_{i=1}^N \mathbf{p}_i^2\right]^\alpha\right\}\mathrm{d}\mathbf{p}_1\cdots\mathrm{d}\mathbf{p}_N$$

$$= \frac{|\mathbb{G}|^N}{(a_ra_ph_c)^{DN}}\frac{2\pi^{\frac{DN}{2}}}{\Gamma\left(\frac{DN}{2}\right)}\int_0^\infty \exp\left\{-\left(\frac{\beta}{2m}t^2\right)^\alpha\right\}t^{DN-1}\,\mathrm{d}t$$

$$= \frac{1}{\alpha}\frac{|\mathbb{G}|^N}{(r^\ominus a_r)^{DN}}\left(\frac{2\pi mk_B\mathsf{T}}{a_p^2 p^{\ominus 2}}\right)^{\frac{DN}{2}}\frac{\Gamma\left(\frac{DN}{2\alpha}\right)}{\Gamma\left(\frac{DN}{2}\right)}, \tag{106}$$

where the integrals (F1) and (F2) have been used, and Eq. (41) in the last step. Inserting the rescaling factors from Eq. (101) and identifying $h_c = r^\ominus p^\ominus = h$ with Planck's constant gives

$$Z_\mathsf{F}(\mathsf{T}, \mathbb{G}, N; H_{\mathbb{G},1/\alpha}) = \frac{|\mathbb{G}|^N}{N!} \left(\frac{2\pi m k_B \mathsf{T}}{h^2}\right)^{\frac{DN}{2}}, \qquad (107)$$

the canonical partition sum of the ideal gas independent of K. The thermodynamic potentials follow from Eq. (91).

VIII. APPLICATION TO SPIN SYSTEMS

A. Infinite range Ising model

A textbook example for unstable interactions in lattice spin systems is the infinite range Ising model with strong coupling. It arises from Eq. (50) by setting

$$n = 1, \quad J_{ij} = J_s, \quad \text{and} \quad J_i = h \qquad (108)$$

for all $i, j = 1, \dots, N \in \mathbb{N}$. The double summation in Eq. (50) extends over all $N(N-1)/2$ pairs of spins. The energy function is then

$$H_\mathbb{G}(\omega) = -J_s \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \omega_i \omega_j - h \sum_{i=1}^{N} \omega_i, \qquad (109)$$

where every Ising spin $\omega_i = \pm 1$ interacts with all other spins with a coupling constant $J_s > 0$. In addition an external field $h \in \mathbb{R}$ acts on every spin.

The weak coupling variant of Eq. (109), the so called Curie-Weiss-Ising model, is an exactly soluble textbook paradigm for the mean-field universality class. It is obtained by replacing J_s with J_w/N in Eq. (109) so that the first term increases as N instead of as N^2. The Gibbs free energy per spin of the weak coupling model reads

$$g(\mathsf{T}, h) = k_B \mathsf{T} \left[\log\left(\frac{1+m}{2}\right)^{\frac{1+m}{2}} + \log\left(\frac{1-m}{2}\right)^{\frac{1-m}{2}} \right]$$
$$- \frac{J_w}{2} m^2 - hm, \qquad (110)$$

where the solution of the celebrated mean-field equation

$$m = \tanh\left(\frac{J_w m + h}{k_B \mathsf{T}}\right) \qquad (111)$$

gives $m = m(\mathsf{T}, h)$ (see Refs. [26,41]). Mean-field critical behavior is expected to apply above the upper critical dimension of realistic models with short range interactions. This is consistent with the observation that interactions with infinite range are related to the $D \to \infty$ limit [26,41] of short range models.

The state space $\Omega_\mathbb{G}$ will here be denoted as Ω_N, because it is discrete and $\mathbb{G}$ plays no role. In fact

$$\Omega_N = \{\omega = (\omega_1, \dots, \omega_N) : \omega_i = \pm 1, i = 1, \dots, N\} \quad (112)$$

is the set of 2^N corners of the N-dimensional hypercube. Let $N_-(\omega)$ and $N_+(\omega)$ denote the number of negative and positive spins in state ω with

$$N = N_+(\omega) + N_-(\omega) \qquad (113)$$

for all $\omega \in \Omega_N$, and let $M : \Omega_N \to \{-N, \dots, N\}$

$$M(\omega) := \sum_{i=1}^{N} \omega_i = N_+(\omega) - N_-(\omega) \qquad (114)$$

denote the total magnetization of the state ω. Then

$$M + N = 2N_+, \qquad (115a)$$

$$M - N = -2N_-, \qquad (115b)$$

and the observation

$$M(\omega)^2 = \left(\sum_{i=1}^{N} \omega_i\right)^2 = N + 2 \sum_{\substack{i=1 \\ i>j}}^{N} \sum_{j=1}^{N} \omega_i \omega_j \qquad (116)$$

allows to express the energy from Eq. (109),

$$H_N(\omega) = -J_s \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j>i}}^{N} \omega_i \omega_j - h \sum_{i=1}^{N} \omega_i$$
$$= H_N(M(\omega)) = -\frac{J_s}{2}(M^2 - N) - hM, \qquad (117)$$

as a function of total magnetization $M = -N, \dots, N$. The ratio

$$m := \frac{M}{N} = 1 - \frac{2N_-}{N} = \frac{2N_+}{N} - 1 \qquad (118)$$

is the magnetization per spin. Here and below, the notation H_N is used instead of $H_\mathbb{G}$, because all spins couple to all spins, and the domain plays no role.

For $h > 0$ the ground state is $\omega^0 = (+1, \dots, +1)$, for $h < 0$ it is $\omega^0 = (-1, \dots, -1)$ [49]. For $h = 0$ there are two states $\omega^0 = (\pm 1, \dots, \pm 1)$ of lowest energy. The ground state magnetizations are $M_N(\omega^0) = \pm N$. The ground state energy is

$$H_N^0 = -\frac{J_s}{2}(N^2 - N) - h\,\mathrm{sgn}(h)\,N \qquad (119)$$

for all $J_s > 0, h \in \mathbb{R}, N \in \mathbb{N}$. Equation (34) shows that the index of stability is $\sigma = 1/\alpha = 2$.

B. Rescaling factors

Contrary to the case of the ideal gas, the system is discrete and has only a finite number of states at fixed N. Therefore, no rescaling is needed and

$$a_\omega = 1 \qquad (120)$$

is used for the rescaling factors. It will be seen that the generalized ensembles lead to existence of the thermodynamic limit and extensive thermodynamic potentials, although the energy diverges as N^2. In conventional Boltzmann-Gibbs theory existence of the thermodynamic limit $N \to \infty$ requires rescaling the strength J/N of the coupling constant [26,41].

C. Microcanonical partition sum

The natural variables in Eq. (117) are the magnetization M and the magnetic field h (see [26]). While M is extensive, h is intensive. The microcanonical partition sum in Eq. (77)

becomes with $\alpha = 1/2$

$$Z_{\mathsf{S}}(E, h, N; H_N) = Z_{\mathsf{S}}(E, h, N) \tag{121}$$

$$= \sum_{\omega \in \Omega_N} \frac{1}{H_N(\omega) - H_N^0} \; \mathsf{h}_{1/2}\left(\frac{E}{H_N(\omega) - H_N^0}\right),$$

where the summation runs over all 2^N spin configurations. The result

$$\mathsf{h}_{1/2}(x) = \frac{x^{-3/2}}{\sqrt{4\pi}} e^{-1/(4x)} \tag{122}$$

is obtained from Eq. (68). With this Eq. (121) becomes

$$Z_{\mathsf{S}}(E, h, N) = \sum_{\omega \in \Omega_N} \sqrt{\frac{H_N(\omega) - H_N^0}{4\pi E^3}}$$

$$\times \exp\left(-\frac{(H_N(\omega) - H^0)}{4E}\right)$$

$$= \sum_{N_+ = 1}^{N} \binom{N}{N_+} \sqrt{\frac{H_N(N_+) - H_N^0}{4\pi E^3}}$$

$$\times \exp\left(-\frac{(H_N(N_+) - H_N^0)}{4E}\right) \tag{123}$$

when the summation over the 2^N spin configurations is written as a summation over the possible values for the number of positive spins. Because of $H_N(N_+ = 0) = H^0$ the term for $N_+ = 0$ vanishes and the summation starts at $N_+ = 1$.

The energy shifted by H_N^0 becomes

$$\widetilde{H_N} = H_N - H_N^0$$

$$= -\frac{J_s}{2}(M^2 - N) - hM + \frac{J_s}{2}(N^2 - N) \pm hN$$

$$= -N^2 \frac{J_s}{2}(m^2 - 1) - hN(m \mp 1), \tag{124}$$

where the upper sign applies for $h > 0$, the lower for $h < 0$. Inserting this into Eq. (123) leads to

$$Z_{\mathsf{S}}(E, h, N) = \sum_{N_+ = 1}^{N} \binom{N}{N_+} \tag{125}$$

$$\times \sqrt{\frac{N^2}{4\pi E^3}\left(-\frac{J_s}{2}(m^2 - 1) - \frac{h}{N}(m \mp 1)\right)}$$

$$\times \exp\left[\frac{N^2}{4E}\left(\frac{J_s}{2}(m^2 - 1) + \frac{h}{N}(m \mp 1)\right)\right],$$

where $m = (2N_+/N) - 1$. For $N, E \to \infty$ one finds using the approximations from Appendix D

$$Z_{\mathsf{S}}(E, h, N) \approx \sum_{N_+ = 1}^{N} \exp\left\{-N\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) \right.\right. \tag{126}$$

$$\left.\left. + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right) + \frac{J_s}{8\mathsf{e}}(1 - m^2)\right]\right\},$$

where $\mathsf{e} = E/N$ is the energy per spin. This finding suggests that the thermodynamic limit exists. For large N the sum is

dominated by the term for which

$$\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right)$$

$$+ \frac{J_s}{8\mathsf{e}}(1 - m^2) \tag{127}$$

is smallest. The saddle point condition reads

$$\text{artanh}(m) - \frac{J_s m}{4\mathsf{e}} = 0 \tag{128a}$$

or

$$m = \tanh\left(\frac{J_s m}{4\mathsf{e}}\right), \tag{128b}$$

where Appendix E has been used. The second derivative of the expression (127), given as

$$\frac{1}{1 - m^2} - \frac{J_s}{4\mathsf{e}} > 0, \tag{129}$$

is positive because

$$\frac{1}{m}\text{artanh}(m) < \frac{1}{1 - m^2} \tag{130}$$

holds for $-1 \leqslant m \leqslant 1$, $m \neq 0$. Thus the solution of Eq. (128) determines the value $N_+ = N(m + 1)/2$ that dominates the summation in Eq. (126).

D. Microcanonical entropy per spin

The thermodynamic limit $N \to \infty$, $E \to \infty$ is taken such that the energy per spin $E/N = \mathsf{e}$ exists. Using Eq. (D4) the entropy per spin becomes in this limit

$$\mathsf{s}(\mathsf{e}, h) = k_B \lim_{\substack{N \to \infty \\ E \to \infty \\ E/N = \mathsf{e}}} \frac{1}{N} \log Z_{\mathsf{S}}(E, h, N) \tag{131}$$

$$= -k_B\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) \right.$$

$$\left. + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right) + \frac{J_s}{8\mathsf{e}}(1 - m^2)\right]$$

with $m = m(\mathsf{e}, h) = m(\mathsf{e})$ given by the solution of Eqs. (128).

For $\mathsf{e} > J_s/4$ the solution of Eqs. (128) is $m = 0$ and the entropy is concave. One finds

$$\mathsf{s}(\mathsf{e}, h) = k_B \log 2 - \frac{k_B J_s}{8\mathsf{e}} \tag{132}$$

for $\mathsf{e} > J_s/4$ and all h. At $\mathsf{e} = J_s/4$ the solution m becomes unstable and at this point one has

$$\mathsf{s}(\mathsf{e}, h)|_{\mathsf{e} = J_s/4} = k_B \log 2 - \frac{k_B}{2}, \tag{133a}$$

$$\frac{\partial \mathsf{s}(\mathsf{e}, h)}{\partial \mathsf{e}}\bigg|_{\mathsf{e} = J_s/4} = \frac{1}{\mathsf{T}} = \frac{2k_B}{J_s}. \tag{133b}$$

For $\mathsf{e} < J_s/4$ the entropy is convex and the specific heat is negative.

The concave hull is given by the straight line

$$\mathsf{s}(\mathsf{e}, h) = \frac{k_B 2(\log 2)^2}{J_s} \, \mathsf{e} \tag{134}$$

connecting the point $(s, e) = (0, 0)$ to the point $(s, e) = (s_c, e_c)$ where

$$e_c = \frac{J_s}{4 \log 2}, \tag{135a}$$

$$s_c = k_B \frac{\log 2}{2}. \tag{135b}$$

The slope

$$\frac{1}{T_c} = \frac{s_c}{e_c} = \frac{k_B}{J_s} 2(\log 2)^2 \tag{136}$$

of the flat section determines the critical temperature T_c of a first order phase transition. The latent heat per spin given by

$$\Delta Q = T_c s_c = \frac{J_s}{4 \log 2} \approx 0.36 J_s \tag{137}$$

is significant. Summarizing

$$s(e, h) = \begin{cases} k_B \log 2 - \frac{k_B J_s}{8e} & \text{for } e \geqslant e_c, h \in \mathbb{R} \\ e \frac{k_B (\log 2)^2}{J_s} & \text{for } e \leqslant e_c, h \in \mathbb{R} \end{cases} \tag{138}$$

is the entropy per spin in equilibrium.

E. Gibbs free energy per spin

The microcanonical temperature is defined by the relation

$$\left. \frac{\partial s}{\partial e} \right|_h = \frac{1}{T} \tag{139}$$

which leads to

$$\frac{1}{T} = -k_B \operatorname{artanh}(m) \left. \frac{\partial m}{\partial e} \right|_h + \frac{k_B J_s m}{4e} \left. \frac{\partial m}{\partial e} \right|_h + \frac{k_B J_s (1 - m^2)}{8e^2}. \tag{140}$$

The first two terms on the right hand side cancel by virtue of Eq. (128a). The resulting relation

$$k_B T J_s (1 - m^2) = 8e^2 \tag{141}$$

is solved for e and inserted into Eqs. (128) to give the condition

$$m = \tanh \left(m \sqrt{\frac{\beta J_s}{2(1 - m^2)}} \right) \tag{142}$$

that the equation of state $m(T, h)$ has to fulfill.

Equation (142) has up to five solutions. The number of solutions is controlled by the slope at $m = 0$ of the argument inside $\tanh(x)$. For

$$\left. \frac{d}{dm} \sqrt{\frac{\beta J_s m^2}{2(1 - m^2)}} \right|_{m=0} = \sqrt{\frac{\beta J_s}{2}} > 1, \tag{143}$$

i.e., for $k_B T < J_s/2$ there exist only two solutions $m = \pm 1$. For $k_B T > J_s/2$ there exist five solutions, two of which are unstable. The three stable solutions are

$$m(T, h) = \begin{cases} \pm 1 & \text{for all } T > 0 \\ 0 & \text{for all } T > J_s/(4k_B). \end{cases} \tag{144}$$

Solving Eq. (142) gives $m = m(T, h)$ and

$$\begin{aligned} s(T, h) = -k_B &\left[\left(\frac{1+m}{2} \right) \log \left(\frac{1+m}{2} \right) \right. \\ &\left. + \left(\frac{1-m}{2} \right) \log \left(\frac{1-m}{2} \right) + \sqrt{\frac{\beta J_s}{8}(1 - m^2)} \right] \\ = &\begin{cases} 0 & \text{for } T < T_c \\ k_B \log 2 - k_B \sqrt{\frac{J_s}{8k_B T}} & \text{for } T > T_c, \end{cases} \end{aligned} \tag{145}$$

where in the last equation it was used that $m = 0$ for $T > T_c$ and $m = \pm 1$ for $T < T_c$ are the only stable solutions of Eq. (142).

The heat capacity per spin is

$$\begin{aligned} c_h(T, h) = &T \left. \frac{\partial s}{\partial T} \right|_h \\ = &\begin{cases} 0 & \text{for } T < T_c, h \in \mathbb{R} \\ \frac{k_B}{4} \sqrt{\frac{J_s}{2k_B T}} & \text{for } T > T_c, h \in \mathbb{R}. \end{cases} \end{aligned} \tag{146}$$

At T_c this gives

$$c_h(T_c, h) = \frac{k_B}{4} \log 2. \tag{147}$$

Relation (141) shows

$$e(T, h) = \begin{cases} 0 & \text{for } T < T_c \\ \sqrt{\frac{J_s k_B T}{8}} & \text{for } T > T_c. \end{cases} \tag{148}$$

Now the thermodynamic definition

$$g(T, h) = e(T, h) - Ts(T, h) \tag{149}$$

gives

$$g(T, h) = \begin{cases} 0 & \text{for } T < T_c \\ \sqrt{\frac{J_s}{2} k_B T} - k_B T \log 2 & \text{for } T > T_c. \end{cases} \tag{150}$$

F. Canonical partition sum

To check the consistency of the general formalism it is important to rederive the same results directly from the canonical ensemble. For $\sigma = 1/\alpha = 2$ the canonical partition sum in Eq. (89) is written as

$$\begin{aligned} Z_F(T, h, N) &= \sum_{\omega \in \Omega_N} e^{-\sqrt{\beta(H_N(\omega) - H_N^0)}} \\ &= \sum_{N_+=1}^{N} \binom{N}{N_+} e^{-\sqrt{\beta(H_N(N_+) - H_N^0)}}, \end{aligned} \tag{151}$$

a sum over N_+. Then

$$Z_F(T, h, N) = \sum_{N_+=1}^{N} \binom{N}{N_+}$$
$$\times \exp\left\{-\sqrt{N^2\beta\left(-\frac{J_s}{2}(m^2-1) - \frac{h}{N}(m \mp 1)\right)}\right\} \tag{152}$$

is the analog of Eq. (125) in the microcanonical computation. For $N \to \infty$ one finds

$$Z_F(T, h, N) \approx \sum_{N_+=1}^{N} \exp\left\{-N\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right)\right.\right.$$
$$\left.\left. + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right) + \sqrt{\frac{\beta J_s}{2}(1-m^2)}\right]\right\} \tag{153}$$

and the largest summand is determined from the saddle point condition

$$\text{artanh}(m) - \frac{\beta J_s m/2}{\sqrt{\beta J_s(1-m^2)/2}} = 0 \tag{154}$$

which is the same as Eq. (142). The thermodynamic limit $N \to \infty$ exists and the Gibbs free energy becomes

$$g(T, h) = -k_B T \lim_{N\to\infty} \frac{1}{N} \log Z_F(T, h, N)$$
$$= k_B T\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right)$$
$$+ k_B T\left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right)$$
$$+ \sqrt{\frac{k_B T J_s}{2}(1-m^2)}, \tag{155}$$

where $m = m(T, h)$ is the solution of Eq. (142). Inserting the stable solutions $m = 0, \pm 1$ from Eq. (144) recovers the specific Gibbs free energy from Eq. (150).

G. Discussion

In conventional Boltzmann-Gibbs theory the thermodynamic limit for the strong coupling model (109) does not exist. Although the energy in Eq. (109) increases as N^2, the calculations above establish existence of the thermodynamic limit. This result demonstrates that the generalized microcanonical and canonical ensembles are suitable to include systems with unstable interactions into the realm of applicability of equilibrium thermodynamics and statistical mechanics.

Physically, in the strong coupling mean-field theory (109) the exchange interaction energy varies as $\sim N^2$, while the contribution from the external field varies only as $\sim N$. In the thermodynamic limit the field h becomes irrelevant for the thermodynamic behavior of the strong coupling model. As a result the magnetization per spin $m = m(e, h) = m(e)$ given by the solution of Eqs. (128) does not depend on h, and hence also the entropy per spin $s = s(e, h) = s(e)$ in Eqs. (138) does not depend on the field h. The thermodynamic behavior is dominated purely by the exchange coupling.

The N^2 dominance of the exchange interaction energy over the field energy gives rise to a novel type of first order collapse transition into the ground state [7]. Its most remarkable feature is the absence of thermodynamic fluctuations in the low energy resp. low temperature phase. Below the critical temperature

$$k_B T_c = \frac{J_s}{2(\log 2)^2} \approx 1.04 J_s \tag{156}$$

the equilibrium state of the system is its ground state. The equilibrium enthalpy per spin, the equilibrium entropy per spin, the equilibrium Gibbs free energy per spin, and the equilibrium heat capacity per spin all vanish below T_c. The set of equilibrium spin configurations below T_c consists only of the ground state, a most unusual result.

At $T = \infty$ the system is in a state with $m = 0$. If energy is extracted to reach e_c or the system is cooled down to T_c, then its equilibrium magnetization per spin $m(e_c, h) = 0$ as well as $m(T_c, h) = 0$ still vanish at the critical point. The barrier to the low temperature phase is huge. The metastable extension of the high temperature phase with $m = 0$ into the low energy phase becomes unstable only at $e = J_s/4 < e_c$ (in the microcanonical calculation) resp. at $T = J_s/(4k_B) < T_c$ (in the canonical calculation). At this point the system must collapse into the ground state by jumping over a temperature resp. an energy gap. At a temperature T_s defined by

$$k_B T_s = \frac{J_s}{8(\log 2)^2} \approx 0.26 J_s \tag{157}$$

the metastable extension of the entropy per spin becomes zero, and it is negative for $T < T_s$. At this same temperature the metastable extension of the high temperature branch of the Gibbs potential G in Eq. (150) has a maximum. The metastable branch of the Gibbs potential for $T < T_c$ ends at $T = 0$. Its end point is a critical point representing an unusual $T = 0$ phase transition. The phase transition has generalized Ehrenfest order $1/2$ in the generalized Ehrenfest classification [10,18]. Such transitions were called anequilibrium transitions in [12].

The ground state with $m = \pm 1$ and without any fluctuations is very stable. This is seen from the fact that it remains a metastable solution of Eq. (142) for all temperatures $T > T_c$.

The phase transition in the strong coupling model differs significantly from the result (110) for the weak coupling model [26,41]. In conventional Boltzmann-Gibbs theory the existence of the thermodynamic limit requires to replace J_s in Eq. (109) with $J_w = J_s/N$ (Ref. [26], Eq. (6.52)). The exchange coupling strength then tends to zero in the $N \to \infty$ limit, so that the interaction energy is of the same order $\sim N$ as the field energy. The thermodynamic potentials for the strong coupling model were compared to the weak coupling model in [6,7]. The results above are identical up to a trivial energy shift of $J_s/2$ to those in [6,7].

In the strong coupling model the (T, h)-phase diagram shows a line of first order phase transitions given by the equation $T = T_c$. This line extends from $h = -\infty$ to $h = +\infty$ without ending in any critical point. This resembles the coexistence line of fluid-solid transitions and supports the view that the transition belongs to another hitherto unknown mean-field universality class.

IX. SUMMARY

Extensivity and existence of the thermodynamic limit in equilibrium statistical mechanics have for a long time restricted its applicability to systems with stable interactions. The extension to unstable interactions introduced in this work lifts this classic restriction.

Traditional statistical mechanics rests on the fundamental Boltzmann-Gibbs postulate. "*The fundamental postulate of statistical mechanics asserts that systems with a large number of particles in thermodynamical equilibrium are described by Gibbs distributions. The question of distinguishing the class of Gibbs distributions by means of some a priori physically natural conditions is extremely important for the mathematical foundations of statistical mechanics*" (Ref. [50], p. 405).

This paper has identified three *a priori* physically natural conditions that distinguish the class of Gibbs distributions. These conditions are (1) divisibility of equilibrium states, (2) extensivity of energy, and (3) independence of isolated systems. These conditions were identified from considering extensivity and stability to be important pillars in the foundations of statistical physics.

The class of distributions distinguished by these three conditions is a one parameter family of distributions characterized by an index of stability σ. The classical Gibbs distributions for stable and tempered interactions are contained as the special case $\sigma = 1$. In addition the extended class contains distributions for unstable interactions where $\sigma \neq 1$.

The one parameter family of distributions leads to a one parameter family of generalized ensembles for stable and unstable systems. These were introduced in Sec. VI. The generalized ensembles were subsequently tested in two cases: first, for ideal gases with constant K-body potentials where the stability index is $\sigma = K$, and second, for the infinite range Ising model (Curie-Weiss-Ising model) with strong coupling where the stability index is $\sigma = 2$. The results confirm the applicability of the generalized ensembles to unstable interactions.

For ideal gases, the generalized unstable ensembles reproduce the thermodynamic potentials of the ideal gas for all values of $\sigma = K \in \mathbb{N}$. While this result was to be expected on physical grounds, the result is unexpected insofar as the thermodynamic limit now depends on the value of σ. The thermodynamic limit is treated as a scaling limit in which position and momentum are rescaled in the Hamilton function.

In the case of the mean-field Ising model with strong coupling, the thermodynamic potentials differ markedly from the weak coupling universality class. An unusual first order collapse transition into a fluctuation free ground state is found indicating the existence of another mean-field universality class. While this result had been obtained earlier [6] based on the author's theory of phase transitions and the ensemble limit [15], the result was doubted [51], because it had not been derived directly from the fundamental postulate of statistical mechanics. Section VIII now closes this gap and provides such a derivation. The results also exhibit a phase transition of generalized Ehrenfest order $1/2$ albeit in the metastable high temperature branch of the Gibbs potential in Eq. (150). It is a critical point at zero temperature. Phase transitions of order less than unity were predicted and named anequilibrium transitions in [12].

In summary, the results of this work enlarge the foundations of statistical mechanics. These extended foundations permit the calculation of thermodynamic potentials for stable as well as unstable systems in a thermodynamic scaling limit.

APPENDIX A: PROBABILITY MEASURES

A probability measure assigns a probability to a (random) event. More precisely, let Ω be a nonempty set interpreted as the set of elementary observations or elementary events. A general nonelementary event is then a subset of Ω. Let $\mathscr{P}(\Omega)$ denote the set of all subsets of Ω (the *power set of* Ω). Probabilities of general events can be defined in a consistent way only on certain classes $\mathscr{A}$ of subsets of Ω. Such classes are specified by the following three conditions:

(i) $\Omega \in \mathscr{A}$.
(ii) With every set in $\mathscr{A}$, also its complement is in $\mathscr{A}$.
(iii) The countable union of sets in $\mathscr{A}$ is in $\mathscr{A}$.

A class $\mathscr{A}$ of subsets of Ω fulfilling these three conditions is called a σ-*algebra*. Let $\mathscr{A} \subset \mathscr{P}(\Omega)$ and let $\mu : \mathscr{A} \to [0, \infty]$ be a set function with $\mu(\emptyset) = 0$. The set function μ is called σ-*additive* if

$$\mu\left(\bigcup_{i=1}^{\infty} A_i\right) = \sum_{i=1}^{\infty} \mu(A_i) \tag{A1}$$

holds for any choice of countably many disjoint sets $A_i \in \mathscr{A}$ with $\bigcup_{i=1}^{\infty} A_i \in \mathscr{A}$. A σ-additive set function is called a *measure*. A measure is called a *probability measure* if $\mu(\Omega) = 1$.

A pair $(\Omega, \mathscr{A})$ consisting of a nonempty set Ω and a σ-algebra $\mathscr{A} \subset \mathscr{P}(\Omega)$ is called a *measurable space*. A triple $(\Omega, \mathscr{A}, \mu)$ consisting of a nonempty set Ω, a σ-algebra $\mathscr{A} \subset \mathscr{P}(\Omega)$, and a measure μ is called a *measure space*. If μ is a probability measure it is called a *probability space*.

An additive set function μ [see Eq. (5)] is called a *content* on $\mathscr{A}$. Examples for a content are the volume $|\mathbb{G}| = V(\mathbb{G})$ and the amount of substance $\mathsf{N}(\mathbb{G})$ of a thermodynamic system $\mathbb{G} \subseteq \mathbb{R}^D$. In that case $\Omega = \mathbb{R}^D$. A content on $\mathscr{A}$ is called *finite* if $\mu(A) < \infty$ for every $A \in \mathscr{A}$. A content on $\mathscr{A}$ is called σ-*finite* if there exists a sequence of sets $A_1, A_2, \ldots \in \mathscr{A}$ such that

$$\Omega = \bigcup_{i=1}^{\infty} A_i \tag{A2}$$

and $\mu(A_i) < \infty$ for all $i \in \mathbb{N}$. For every content μ Eq. (5) implies the inclusion-exclusion formula [52]. It is written here in the notation of Sec. III for the amount of substance as

$$\mathsf{N}(\mathbb{G}) = \sum_{\mathfrak{h} \in \mathscr{P}(N)} (-1)^{|\mathfrak{h}|-1} \mathsf{N}\left(\bigcap_{i \in \mathfrak{h}} \mathbb{G}_i\right), \tag{A3}$$

where $\mathscr{P}(N)$ is shorthand for $\mathscr{P}(\{1, \dots, N\})$ and $|\mathfrak{h}|$ is the cardinality of $\mathfrak{h} \in \mathscr{P}(N)$.

APPENDIX B: CONVEX RING

The *convex ring* is defined as the set of finite unions of convex and compact sets [53]

$$\mathscr{R} = \left\{ \mathbb{G} \subset \mathbb{R}^D : \mathbb{G} = \bigcup_{i=1}^{n} \mathbb{K}_i \text{ with } n < \infty \text{ and} \right.$$

$$\left. \mathbb{K}_i \subset \mathbb{R}^D \text{ convex and compact} \right\}. \quad \text{(B1)}$$

Note that $\mathbb{G}_1, \mathbb{G}_2 \in \mathscr{R}$ implies $\mathbb{G}_1 \cup \mathbb{G}_2 \in \mathscr{R}$ and $\mathbb{G}_1 \cap \mathbb{G}_2 \in \mathscr{R}$. The convex ring $\mathscr{R}$ contains also nonconvex sets. In fact, $\mathscr{R}$ is a dense subset of the metric space $\mathscr{C}$ of all compact subsets of $\mathbb{R}^D$ [53]. The distance between two sets in $\mathscr{C}$ is defined by

$$d(\mathbb{G}_1, \mathbb{G}_2) = \max \left\{ \sup_{x \in \mathbb{G}_1} \inf_{y \in \mathbb{G}_2} |x - y|, \sup_{x \in \mathbb{G}_2} \inf_{y \in \mathbb{G}_1} |x - y| \right\} \quad \text{(B2)}$$

for $\mathbb{G}_1, \mathbb{G}_2 \in \mathscr{C} \setminus \{\emptyset\}$ and by $d(\emptyset, \emptyset) = 0$ and $d(\mathbb{G}, \emptyset) = d(\emptyset, \mathbb{G}) = \infty$ for the empty set and $\mathbb{G} \in \mathscr{C} \setminus \{\emptyset\}$. It defines the (Hausdorff) metric on $\mathscr{C}$.

APPENDIX C: FUNCTIONAL FORM OF ENERGY DISTRIBUTION

Another method to identify $w(E)$ as a special function is based on the relation

$$\mathscr{M}\{f(x)\}(s) = \frac{\mathscr{M}\{\mathscr{L}\{f(x)\}(u)\}(1-s)}{\Gamma(1-s)} \quad \text{(C1)}$$

between the Laplace transform and the Mellin transform

$$\mathscr{M}\{f(x)\}(s) = \int_0^{\infty} x^{s-1} f(t) \, dx \quad \text{(C2)}$$

of a function $f(x)$. Using the Mellin transform [54]

$$\mathscr{M}\{e^{-Bx^{\alpha}}\}(s) = \frac{\Gamma(s/\alpha)}{\alpha B^{s/\alpha}} \quad \text{(C3)}$$

valid for $\alpha > 0$ and $\text{Re}\,s > 0$ it follows that

$$\mathscr{M}\{w(u; \alpha, B)\}(s) = \frac{1}{\alpha B^{(1-s)/\alpha}} \frac{\Gamma((1-s)/\alpha)}{\Gamma(1-s)}. \quad \text{(C4)}$$

The general relation $\mathscr{M}\{x^{-1} f(x^{-1})\}(s) = \mathscr{M}\{f(x)\}(1-s)$ then implies

$$\mathscr{M}\{E^{-1} w(E^{-1}; \alpha, B)\}(s) = \frac{1}{\alpha B^{s/\alpha}} \frac{\Gamma(s/\alpha)}{\Gamma(s)} \quad \text{(C5)}$$

which leads to

$$E^{-1} w(E^{-1}; \alpha, B) = \frac{1}{\alpha} H_{11}^{10} \left(B^{1/\alpha} E \left| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix} \right. \right) \quad \text{(C6)}$$

by identification with H functions [45]. Using the series expansion (Ref. [45], p. 125, Eq. (180))

$$H_{11}^{10} \left(x \left| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix} \right. \right) = \alpha \sum_{k=0}^{\infty} \frac{(-1)^k x^{\alpha k}}{k! \, \Gamma(-\alpha k)} \quad \text{(C7)}$$

and noting that the first term in this series vanishes reproduces the result of Eq. (65).

APPENDIX D: STIRLING'S FORMULA

Stirling's formula from Ref. [55] (p. 78, formula 6.1.37) is

$$\Gamma(z) \approx e^{-z} z^{z-\frac{1}{2}} (2\pi)^{\frac{1}{2}} \left(1 + \frac{1}{12z} + \frac{1}{288z^2} - \cdots \right) \quad \text{(D1)}$$

for $z \to \infty$ in $|\arg z| < \pi$, or with $n! = \Gamma(n+1) = n\Gamma(n)$

$$n! \approx e^{-n} n^n \sqrt{2\pi n} \quad \text{(D2)}$$

for $n \to \infty$. For $n \to \infty, k \to \infty$ with $k/n \to c = \text{const}$

$$\begin{aligned} \binom{n}{k} &= \frac{n!}{k!(n-k)!} \\ &\approx \sqrt{\frac{n}{2\pi k(n-k)}} \; n^n k^{-k} (n-k)^{k-n} \\ &= \frac{1}{\sqrt{2\pi n}} \left(\frac{k}{n} \right)^{-k-\frac{1}{2}} \left(1 - \frac{k}{n} \right)^{k-n-\frac{1}{2}} \\ &= \frac{1}{\sqrt{2\pi n}} \left(\frac{k}{n} \right)^{-n(\frac{k}{n} + \frac{1}{2n})} \left(1 - \frac{k}{n} \right)^{-n(1 - \frac{k}{n} + \frac{1}{2n})} \end{aligned} \quad \text{(D3)}$$

follows from Stirling's formula (D2). Thus

$$\log \binom{n}{k} \approx -n[c \log c + (1-c) \log(1-c)] \quad \text{(D4)}$$

for $n \to \infty, k \to \infty$ with $k/n \to c = \text{const}$.

APPENDIX E: AUXILIARY CALCULATION

$$\begin{aligned} &\frac{\partial}{\partial m} \left[\left(\frac{1+m}{2} \right) \log \left(\frac{1+m}{2} \right) + \left(\frac{1-m}{2} \right) \log \left(\frac{1-m}{2} \right) \right] \\ &= \frac{1}{2} \left[\log \left(\frac{1+m}{2} \right) + 1 \right] - \frac{1}{2} \left[\log \left(\frac{1-m}{2} \right) + 1 \right] \\ &= \frac{1}{2} \log \left(\frac{1+m}{1-m} \right) = \text{artanh}(m). \end{aligned} \quad \text{(E1)}$$

APPENDIX F: SOME INTEGRALS

$$\int_0^{\infty} x^{\beta-1} e^{-Cx^{\alpha}} dx = \frac{1}{\alpha} C^{-\beta/\alpha} \Gamma \left(\frac{\beta}{\alpha} \right), \quad \text{(F1)}$$

$$\begin{aligned} &\int \cdots \int f \left(\sqrt{x_1^2 + \cdots + x_n^2} \right) dx_1 \cdots dx_n \\ &= \frac{n \pi^{n/2}}{\Gamma \left(\frac{n}{2} + 1 \right)} \int_0^{\infty} f(r) r^{n-1} dr, \end{aligned} \quad \text{(F2)}$$

$$\int_0^{\infty} x^{z-1} H_{11}^{10} \left(cx \left| \begin{matrix} (0, 1) \\ (0, 1/\alpha) \end{matrix} \right. \right) dx = c^{-z} \frac{\Gamma(z/\alpha)}{\Gamma(z)}. \quad \text{(F3)}$$

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