

From thermodynamics to quantum theory.

Part I: Equilibrium

Arnold Neumaier
Institut für Mathematik, Universität Wien
Strudlhofgasse 4, A-1090 Wien, Austria
email: neumcma.univie.ac.at

Abstract. In this paper, an elementary and self-contained axiomatic treatment is given of equilibrium thermodynamics including fluctuations. Among other things, this leads to a natural explanation of the Hilbert space underlying quantum physics, using only a simple quantization condition related to the third law of thermodynamics.

Preliminary version, February 1994

Keywords: Information, equilibrium thermodynamics, expectation, ensemble, density, entropy, Euler equation, partition function, second law of thermodynamics, energy dissipation, quantization, Hilbert space, quantum logic, probability, fluctuations

PACS-1990 Classification:

primary 64.10.+h, secondary 05.40.+j, 82.60.Hc

Introduction

This is the first of a sequence of papers designed to give a mathematically elementary and philosophically consistent foundation of modern theoretical physics. It is an attempt to reconsider, from a more modern point of view, Hilbert's [8] 6th problem of axiomatization of theoretical physics. It is an attempt only since at the present stage of development, I have not yet tried to achieve full mathematical rigor everywhere. The main reason is that apparently details in the axioms (concerning topological finesses) determine the generality of the theory. To find out which generality will be necessary, I felt it is important to first have a semi-rigorous version which incorporates all the major applications – this is already a huge project –, and to leave the rigorous formulation of all details to a later stage.

This first paper is devoted to “0-dimensional” physics: equilibrium situations where neither time nor space play a role. Subsequent papers will discuss 1-dimensional physics (where variables are time- but not space-dependent, as e.g. in stirred chemical reactions) and 4-dimensional physics (field theory). Since the present paper discusses equilibrium only, the distinguished role of the Hamiltonian does not become apparent; the discussion of dynamics is central, however, for the later papers. The sequence of papers is the result of continued efforts to read between the lines of standard treatises of thermodynamics and statistical mechanics, and to state explicitly what I found.

From a few basic assumptions the full structure of phenomenological thermodynamics and the general structure of statistical mechanics is recovered, without the excessive formalism needed to do actual statistical mechanics calculations. One might describe the paper as an attempt to treat statistical mechanics “without mechanics” and “without probability”, and C^* -Algebras “without functional analysis”. This leads to great conceptual simplifications, and allows one to postpone the standard machinery to a later stage where one actually wants to do quantitative predictions of macroscopic properties from microscopic assumptions.

I think it is worthwhile to have the structural properties of physical theories spelled out independently. This allows one to focus attention on the simplicity and beauty of physics, which is often hidden in a jungle of techniques for estimating or calculating approximations for quantities of interests.

In our setting, many known things appear in a new perspective, and sometimes get a slightly different interpretation. A prominent feature of our presentation is that hardly any distinction is needed between classical and quantum physics; indeed, one can say that, from our perspective, the world is nearly classical. All concepts introduced (even quantization) are valid in the same way for classical systems as for quantum systems.

We try to explain things in a manner that removes several philosophical paradoxes about the foundations of physics, concerning the statistics of unique objects like “the universe”, the role of the second law of thermodynamics (the entropy of the universe need *not* increase!), the relevance of the “collapse of the wave function”, and the emergence of probabilities as expected relative frequencies.

Note that, in contrast to other treatments which relate information theory and thermodynamics (e.g. Jaynes [12], Haken [9]), we do not *assume* the basic thermodynamical laws and relations but *derive* them from simple definitions.

Another novel feature is the fact that, in contrast to most other approaches known so far, our approach need not *postulate in advance* a Hilbert space for treating quantum mechanics, but instead *constructs* this Hilbert space as a consequence of a very natural quantization assumption related to the third law of thermodynamics. This is much more intuitive than constructions based on quantum logic (e.g. Ludwig [16]), which, in our setting, would appear as a consequence of the theory rather than an assumption. (But since we have nothing new to contribute here, this is not discussed in detail.)

The paper is organized as follows: Section 1 has an introductory character, and gives an intuitive meaning to (what is in later sections the) entropy as a quantity (i.e. an operator) beyond the usual interpretation of its expectation as a measure of lack of information. Section 2 gives philosophical arguments intended to show the similarity of the simple system considered in Section 1 to the general case treated later. Section 3 introduces the basic axioms for quantities (our formal versions of observables, but slightly more general), states and ensembles, and proves a few basic results. Section 4 introduces equilibrium ensembles by means of the Euler equation, and shows that the first law of thermodynamics follows by taking expectations. Section 5 compares equilibrium ensembles with arbitrary ensembles and deduces the second law and other variational inequalities. Section 6 introduces the concept of quantization needed to derive the third law, and shows that it naturally leads to a Hilbert space and to the traditional quantum mechanical formalism. Section 7 derives the probability interpretation and the conditions under which classical (Boolean) logic is valid. Finally, Section 8 shows that the basic relations relating fluctuations to response functions follow naturally in our approach. The Appendix contains proofs of some more technical results needed in the main text.

1. Information deficit

To motivate the formal concepts introduced in Section 3 (and their interpretation) we consider in this section a simple (stationary) device which, in regular intervals, delivers a reading n from a countable set \mathcal{N} of possible readings. For example, the device might count the number of events of a certain kind in fixed periods of time; then $\mathcal{N} = \{0, 1, 2, \dots\}$.

We suppose that by observing the device in action for some time, we are led to some conjecture about the expected relative frequencies ρ_n of readings $n \in \mathcal{N}$, and suppose that these relative frequencies are independent of time. (If \mathcal{N} is finite and not too large, we might take averages and wait until these “stabilize to our satisfaction”; if \mathcal{N} is large or infinite, most $n \in \mathcal{N}$ will not have been observed, and our conjecture must depend on “educated guesses”. For the moment, we ignore this subjectiveness.)

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

$$(1) \quad \rho_n > 0 \text{ for all } n \in \mathcal{N},$$

and *some* reading occurs with certainty:

$$(2) \quad \sum_{n \in \mathcal{N}} \rho_n = 1.$$

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

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

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

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

$$(3) \quad \sum_{n \in \mathcal{N}} 2^{-Q_n} \leq 1.$$

It is not difficult to construct a strategy realizing the Q_n whenever (3) holds.

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

$$(4) \quad \bar{Q} = \sum_{n \in \mathcal{N}} Q_n \rho_n.$$

To simplify notation, we introduce the abbreviation

$$(5) \quad \text{tr } A := \sum_{n \in \mathcal{N}} A_n \quad (\text{read "trace A"})$$

for every quantity A indexed by \mathcal{N} , and we use the convention that inequalities, operations and functions of such quantities are understood componentwise. Then we can rewrite (1)–(4) as

$$(6) \quad \rho > 0, \quad \text{tr } \rho = 1,$$

$$(7) \quad \bar{Q} = \text{tr } (Q\rho), \quad \text{tr } (2^{-Q}) \leq 1.$$

Moreover, as for the average number of questions,

$$(8) \quad \bar{A} := \text{tr } (A\rho).$$

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

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

THEOREM 1.1. *Let*

$$(9) \quad S := -\bar{k} \log \rho, \text{ where } \bar{k} = \frac{1}{\log 2}.$$

Then $\bar{Q} \geq \bar{S}$, *with equality if and only if* $Q = S$.

PROOF. (9) implies $\log \rho = -S \log 2$, hence $\rho = 2^{-S}$. Therefore

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

with equality iff $S = Q$. Thus

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

and

$$\begin{aligned} \bar{S} - \bar{Q} &= \text{tr } \rho(S-Q) \leq \text{tr } \bar{k}(2^{-Q} - \rho) \\ &= \bar{k} \text{tr } 2^{-Q} - \bar{k} \text{tr } \rho \leq \bar{k} - \bar{k} = 0. \end{aligned}$$

Hence $\bar{Q} \geq \bar{S}$, and equality holds iff $Q = S$. \square

Note that $Q = S$ defines an admissible strategy since

$$\sum_{n \in \mathcal{N}} 2^{-S_n} = \text{tr } 2^{-S} = \text{tr } \rho = 1,$$

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

$$(10) \quad \bar{S} = \text{tr } (S\rho) = -\bar{k} \text{tr } (\rho \log \rho)$$

of questions needed in an optimal decision strategy may be called the *expected information deficit* of the device (w.r. to our conjecture about relative frequencies).

This name is more suggestive than the commonly used name *information* which invites linguistic paradoxes since ordinary language associates with information a connotation of relevance or quality which is absent here. (An important book on information by Brillouin [2] emphasizes this very carefully, by distinguishing absolute information from its human value or meaning.) In particular, the expected information deficit says nothing at all about the quality of the information

contained in the summary ρ of our past observations. An inappropriate ρ can have arbitrarily small information deficit and still give false account of reality. E.g., if for some small $\varepsilon > 0$,

$$(11) \quad \rho_n = \varepsilon^{n-1}(1 - \varepsilon) \quad \text{for } n = 1, 2, \dots,$$

expressing that the reading is expected to be nearly always 1 ($\rho_1 = 1 - \varepsilon$) and hardly ever large, then

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

Thus the expected information deficit can be made very small by the choice (11) with small ε , independent of whether this choice corresponds to the known facts. The real information value of ρ therefore rather depends on the care with which the past observations were interpreted, which is a matter of data analysis and not of our model of the device. If this is done badly, our expectations will simply not be matched by reality.

Note that as an average of nonnegative numbers, the expected information deficit is always nonnegative,

$$(12) \quad \bar{S} \geq 0.$$

For future use, let us also note that (9) implies the relation

$$(13) \quad \rho = e^{-S/k}$$

which automatically encompasses the positivity condition (1), and yields

$$(14) \quad \text{tr } e^{-S/k} = \text{tr } \rho = 1.$$

2. Philosophical interlude

*Our knowledge is patchwork, and
our predictive power is patchwork.
(New Testament, 1 Cor. 13:9)*

It is my conviction that the interface between model and reality in physics (and in all natural sciences) is very much like in the simple example discussed above, though more complicated. All our scientific knowledge is based on past observation, and only gives rise to conjectures about the future – this is analogous to our tentative choice of ρ . Mathematical consistency requires that our choices are constrained by some formal laws – analogous to the constraints (1) and (2). When we want to predict something – like the number of questions needed – the true answer depends on knowledge we do not have, and we can calculate at best approximations – like the averages in (4) – whose accuracy can be estimated using statistical techniques (assuming that the quality of our models is good).

This implies that we must distinguish between *quantities* (which are formal concepts of what can be measured) and *numbers* (which are the results of measurements themselves); some quantities which are constant by the nature of the concept considered may behave just like numbers. Comparison with experiment exclusively concerns *expectations* of quantities (the formalized version of averages). It is remarkable that, with only very little additional input, this conceptual distinction allows one to derive the classical theory of equilibrium thermodynamics and many qualitative results traditionally accessible only through statistical mechanics.

In the next section, we shall introduce axiomatically concepts inspired by (but more general than those of) the example in Section 1, and prove some simple consequences and some auxiliary results needed later. To avoid an excessive mathematical apparatus we do not add axioms relating to domains of definition, continuity properties and similar things, though these would be necessary for a rigorous treatment. This has the consequence that some proofs are given only under additional assumptions, but the level of formal precision is at least that of most treatments of theoretical physics. Moreover, when the algebra of quantities is finite-dimensional, all proofs are valid rigorously as stated. (In fact, it can be shown that everything already holds rigorously when this algebra is embeddable into a C^* -algebra; but the applications to quantum mechanics require weaker conditions that allow certain unbounded operators to occur, and at present it is not yet clear to me what precisely is needed to rigorously recover the full mathematical structure of quantum statistical mechanics. Moreover, unlike our nearly trivial axioms, the C^* -algebra axioms have no intuitive physical basis, but are abstracted from mathematical properties of algebras of operators on Hilbert spaces.)

It must be emphasized that expectations are primarily properties of the state assigned to a system and *not* of reality itself, just as in our example, ρ (which defines the average) depends on our assessment of reality, which in turn depends on the assumed state of the device (i.e. its input and internal parameters). Thus *states*, which will be defined as expectation mappings, only express our *conjectures* (or even prejudice) about reality, and must be brought into agreement with reality by what is called (passive) *measurement* or (active) *preparation of a state*. In actual practice, states are always abstractions from reality accurate only to a certain extent, and this accuracy is assessed by a measurement-assisted subjective interpretation of reality.

From a practical point of view, theory defines what an object is: A gas is considered as ideal gas, and a solid as a crystal, if it behaves to our satisfaction as a model of an ideal gas, or a crystal, predicts. Thus, in practice, states are *not* prepared by what, in the traditional foundation of quantum mechanics, are known as ideal measurements, but instead by well-informed prejudice concerning one's equipment! We know (or rather assume on the basis of past experience, claims of manufacturers, etc.) that certain materials or machines reliably produce (to our satisfaction, or to the satisfaction of others, whom we trust, who checked that certain norms are satisfied) states that (for the purpose of the experiment or application in mind) depend only on variables that are accounted for in our theory and that are either fixed or controllable (again to our satisfaction). If we are careless or credulous, our expectations will simply not be matched by reality.

Unfortunately, this interface between *what we understand* and *what is*, between model and reality, between theory and experiment, between calculated expectations and measurements always remains a subjective matter ultimately based on trust in measurement devices, apparatus specifications, published data, etc., or perhaps rather based on trust in the people (including ourselves) responsible for them. The strength of theoretical physics lies in the fact that it can ignore this subjective side by assuming states to be *given*, which allows one to calculate expectations from well-defined assumptions. The weakness of theoretical physics lies in the impossibility to objectively verify these assumptions; comparison with reality always rests on trust in subjective aspects of observation and communication. Science is possible only because (and in as much as) it is possible to make these subjective aspects less influential by training people to adhere to high standards of precision, carefulness and truthfulness.

Since these limitations are a built-in part of our axiomatic treatment, the latter gives a satisfactory account for the well-known problem of induction. It is an undeniable fact that any regularity or structure in our world can be *discovered* by means of induction; diligent observation and good theory allows us to *formulate*

the observed regularities as mathematical models. But nothing can *guarantee* that these models are true, even when truth is restricted to “within the specified accuracy”. (Shall I prove that you have eternal life? You experienced all your past birthdays, without a single exception. The most natural model explaining this is that you can rely on that this will go on for ever!! But, of course, this proves nothing.) Induction works in physics *because nature is so highly structured*, and *not* for logical reasons.

The present setting makes this gap between model and reality very explicit by the concept of expectation, and frees theoretical physics from philosophical riddles by a careful cut just at the point where objective expectations and their subjective interpretation interact. In this sense, this paper can be viewed as a mathematical commentary on the statement of H. Margenau [17]: “Measurement is ... the contact of reason with nature.”

The three volume work *Foundations of Measurements* [13, 21, 15] gives a comprehensive survey of – partially successful – attempts to extend the realm of objectivity further by axiomatizing the measurement process in classical physics; the problems involved for the quantum case are well covered in the reprint collection of Wheeler & Zurek [23]. However, one cannot avoid making the transition to subjective judgment at *some* stage, and the setting proposed in the present paper has the great advantage of simplicity.

3. Quantities and ensembles

Though in thermodynamics, everything remains real, our axioms will be formulated using complex numbers. This is done in order to allow later applications to quantum physics – foreshadowed by the use of the trace notation (5). Indeed, one can interpret the observables of quantum theory as quantities in the present sense, though there are many other (not self-adjoint) operators which are quantities, but not observables.

In our axiomatic treatment, *quantities* are primitive objects such that the sum and the product of quantities is again a quantity, and there is an operation $*$ generalizing complex conjugation; a quantity A is called *Hermitian* if $A^* = A$. There is also a complex-valued *trace* defined for some of the quantities. We denote by E the set of all quantities and by E_0 the set of quantities for which the trace exists.

Operations on quantities and traces are required to satisfy a few simple rules; they are called *axioms* since we take them as a formal starting point without making any further demands on the nature of the symbols we are using. It is probably easiest to think of quantities as square matrices, with the usual trace.

Note that for qualitative or phenomenological aspects of the theory there is no need to know any details of how to calculate traces of quantities; this is only needed if one wants to calculate macroscopic properties from microscopic assumptions. In this respect, the situation is quite similar to the traditional axiomatic treatment of real numbers: The axioms specify the permitted ways to handle formulas involving these numbers; and this is enough to derive calculus, say, without the need to specify either what real numbers *are* or algorithmic rules for addition, multiplication and division. Of course, the latter are needed when one wants to do specific calculations but not while one tries to get insight into a problem. And as the development of calculators has shown, the capacity for understanding theory and that for knowing the best ways of calculation need not even reside in the same person.

3.1. Axioms for quantities.

- (Q1) $C \subseteq E$, i.e. complex numbers are special quantities, where addition, multiplication and conjugation have their traditional meaning.
- (Q2) $(AB)C = A(BC)$, $\alpha A = A\alpha$, $0A = 0$, $1A = A$.
- (Q3) $(A + B) + C = A + (B + C)$; $A(B + C) = AB + AC$, $A + 0 = A$.
- (Q4) $A^{**} = A$, $(AB)^* = B^*A^*$, $(A + B)^* = A^* + B^*$.

Here $A, B, C \in E$ and $\alpha \in C$ are arbitrary.

3.2. Axioms for the trace.

- (T1) $\text{tr} (A + B) = \text{tr} A + \text{tr} B$.
 (T2) $\text{tr} (\alpha A) = \alpha \text{tr} A$ for $\alpha \in \mathbb{C}$.
 (T3) $\text{tr} (AB) = \text{tr} (BA)$ when one side is defined.
 (T4) $\text{tr} (AA^*) > 0$ for $A \neq 0$.

We shall call a set E with operations satisfying (Q1)–(Q4) and a trace functional on a linear subspace E_0 of E satisfying (T1)–(T4) an *expectation algebra*. One can introduce the traditional notation

$$\begin{aligned} -A &:= (-1)A, & A - B &:= A + (-B), \\ A^0 &:= 1, & A^l &:= A^{l-1} \cdot A \quad (l = 1, 2, \dots). \end{aligned}$$

We shall also assume that a notion of limit is defined which allows one to make sense of infinite series and in particular of the *exponential function*

$$e^A := \sum_{l \geq 0} \frac{A^l}{l!},$$

defined for all quantities A for which this sum converges. Note that

- (15) $(e^A)^l = e^{Al}$ for $l = 0, 1, 2, \dots$,
 (16) $e^{A+B} = e^A e^B$ if A and B commute ,
 (17) $(e^A)^* = e^{(A^*)}$.

Our axioms are motivated from the wish to be as general as possible while still preserving the ability to manipulate quantities in the manner familiar from matrix algebra. Indeed, the algebra $\bar{E} = \mathbb{C}^{m \times m}$ of all complex $m \times m$ -matrices is an important example of an expectation algebra, used to describe quantum mechanical systems with only a finite number m of relevant energy levels. (Similar axioms have been proposed, e.g., by Dirac [3] and Thirring [22].)

Note that we assume commutativity only between numbers and quantities, and cyclic commutativity within the trace; e.g. $\text{tr} (ABC) = \text{tr} (BCA) = \text{tr} (CAB)$ by (T3), while, in general, $\text{tr} (ABC) \neq \text{tr} (BAC)$. However, commutativity of the addition is a consequence of our other assumption:

PROPOSITION 3.1. *For all quantities $A, B, C \in E$,*

- (Q5) $A - A = 0$,
(Q6) $A + B = B + A$,
(Q7) $(A + B)C = AC + BC$.

PROOF.

- (Q6): Let $C := -A + B$. Then $-C = (-1)((-1)A + B) = (-1)(-1)A + (-1)B = A - B$, so that $A + B = A + (C - C) + B = (A + C) + (-C + B) = (A - A + B) + (A - B + B) = B + A$.
(Q7): $(A + B)C = ((A + B)C)^{**} = (C^*(A + B)^*)^* = (C^*(A^* + B^*))^* = (C^*A^* + C^*B^*)^* = (C^*A^*)^* + (C^*B^*)^* = A^{**}C^{**} + B^{**}C^{**} = AC + BC$.
(Q5): $A - A = 1A - 1A = (1 - 1)A = 0A = 0$, using (Q7).

□

Thus, in conventional terminology (see. e.g. Rickart [20]), E is a $*$ -algebra with unity, but not necessarily with a commutative multiplication. But as the expectation algebra $E = C^{m \times m}$ shows, E may have zero divisors, and not every nonzero quantity need have an inverse. Therefore, in the manipulation of formulas, precisely the same precautions must be taken as in ordinary matrix algebra.

An expectation algebra (together with a physical interpretation of a generating set of quantities) characterizes a *physical system* modeling a class of experimental situations. A particular experimental situation (at a given place and time) is then modeled by a *state* of the system, i.e., a prescription of how to calculate expectations of quantities that can be compared with experiment. We demand some simple properties (abstracted from the example in Section 1).

3.3. Definition. A *state* is a mapping that assigns to quantities A in some linear subspace of E an *expectation* $\langle A \rangle = \overline{A} \in C$ such that

- (E1) $\langle 1 \rangle = 1$,
(E2) $\langle \alpha A \rangle = \alpha \langle A \rangle$ for $\alpha \in C$,
(E3) $\langle A + B \rangle = \langle A \rangle + \langle B \rangle$,
(E4) $\langle AA^* \rangle \geq 0$.

We emphasize that *numbers* are just those quantities that can be pulled out of traces and expectations via (T2) and (E2). In particular, this holds for all expectations of quantities, since these are numbers by definition.

Note that there is no need to interpret expectation as an average (though this is the case in some applications); the expectation of a quantity A is simply a value near which we expect the measured value for A . As a measure of the accuracy to which we may expect this nearness to hold one can calculate the *standard deviation*

$$(18) \quad \sigma(A) := \sqrt{\langle (A - \bar{A})(A - \bar{A})^* \rangle};$$

(E4) ensures that $\sigma(A)$ is a nonnegative real number.

Trace and expectation behave naturally under complex conjugation:

PROPOSITION 3.2.

(i) For any quantity A , the quantities

$$\operatorname{Re} A := \frac{1}{2}(A + A^*), \quad \operatorname{Im} A := \frac{1}{2}(A - A^*)$$

are Hermitean, and

$$A = \operatorname{Re} A + i \operatorname{Im} A.$$

(ii) If A is Hermitean, $\operatorname{tr} A$ is real.

(iii) $\operatorname{tr} (A^*) = (\operatorname{tr} A)^*$.

(iv) For any state, $\langle A^* \rangle = \langle A \rangle^*$, and for Hermitean A , $\langle A^* \rangle$ is real.

PROOF. (i) is trivial.

(ii) If A is Hermitean, the number

$$\alpha := 4 \operatorname{tr} A = \operatorname{tr} (A + 1)(A + 1)^* - \operatorname{tr} (A - 1)(A - 1)^*$$

is, by (T3), the difference of two nonnegative numbers. Hence α is real, and so is $\operatorname{tr} A = \alpha/4$.

(iii) holds since by (i) and (ii),

$$(\operatorname{tr} A)^* = \operatorname{tr} (\operatorname{Re} A + i \operatorname{Im} A)^* = \operatorname{tr} \operatorname{Re} A - i \operatorname{tr} \operatorname{Im} A,$$

hence

$$(\operatorname{tr} A)^* = \operatorname{tr} (\operatorname{Re} A - i \operatorname{Im} A) = \operatorname{tr} A^*.$$

Here i denotes the square root of -1 .

(iv) follows in the same way as (ii) and (iii). \square

In particular, since Hermitean quantities have real expectations, and since real-valued (analytic) functions of Hermitean quantities are Hermitean, too (consider the power series expansion!), it is natural to model by Hermitean quantities all physical variables which take real values only.

Physical systems have a large variety of states, not all of them of the same interest. A large (but already restricted) class of states, namely those of interest for thermodynamics, arise in the following way:

THEOREM 3.3. *For any Hermitean quantity B with*

$$(19) \quad Z := \text{tr } e^{-B} < \infty,$$

the mapping defined by

$$(20) \quad \langle A \rangle := \text{tr } (A\rho),$$

where

$$(21) \quad \rho = \frac{1}{Z} e^{-B},$$

is a state.

PROOF. (E1) holds since $\langle 1 \rangle = \text{tr } \rho = \text{tr } \frac{1}{Z} e^{-B} = \frac{1}{Z} \text{tr } e^{-B} = 1$, and (E2), (E3) are obvious.

To prove (E4), let $C := e^{-B/2} A$. Then $A = e^{B/2} C$ and $A^* = C^* (e^{B/2})^* = C^* e^{B/2}$ since B is Hermitean. Therefore

$$\begin{aligned} \langle AA^* \rangle &= \text{tr } (AA^* \rho) = \frac{1}{Z} \text{tr } AA^* e^{-B} \\ &= \frac{1}{Z} \text{tr } e^{B/2} C C^* e^{B/2} e^{-B} = \frac{1}{Z} \text{tr } C C^* e^{B/2} e^{-B} e^{B/2} \\ &= \frac{1}{Z} \text{tr } C C^* \geq 0. \end{aligned}$$

□

3.4. Definition. A state of the form as in Theorem 3.3 is called an *ensemble* with *density* ρ and *entropy*

$$(22) \quad S := \bar{k}(B + \log Z).$$

Here \bar{k} is the so-called *Boltzmann constant*; it is fixed once and for all and defines the units in which the entropy is measured. In traditional macroscopic units, the Boltzmann constant is very tiny,

$$\hbar \approx 1.38 \cdot 10^{-23} \text{ J/K}.$$

However, by a change of units we can enforce any value of \hbar . In particular, if we choose $\hbar = 1/\log 2$ then the next proposition shows that ensembles are the correct generalization of the situation of Section 1.

PROPOSITION 3.4. *For an ensemble with (Hermitean) entropy S , the density ρ is given by*

$$(23) \quad \rho = e^{-S/\hbar}.$$

In particular, ρ is Hermitean, and

$$(24) \quad \text{tr } e^{-S/\hbar} = \text{tr } \rho = 1.$$

PROOF. $\rho = \frac{1}{Z} e^{-B} = e^{-B - \log Z} = e^{-S/\hbar}$. \square

(23) implies that when the density ρ is given, the entropy takes the form

$$(25) \quad S = -\hbar \log \rho.$$

Thus in order that (20) defines an ensemble, $\log \rho$ must exist and be Hermitean; this corresponds to the positivity condition of Section 1. If this holds and $\text{tr } \rho = 1$ then the state defined by

$$(26) \quad \bar{A} = \langle A \rangle := \text{tr } (A\rho).$$

is indeed an ensemble with entropy (25) (use $B = S/\hbar = -\log \rho$ in Theorem 3.3 and note that $Z = 1$).

Note that an ensemble is just a special way of defining expectations. In particular, and in contrast to traditional interpretations of statistical mechanics, there is no need to postulate the existence of infinitely many hypothetical repetitions of an experiment (which originally gave the ensemble its name)! For example, it is now perfectly consistent to talk about the entropy of the universe, though the latter is unique (if it refers to everything that exists).

The calculation of the partition function Z and of expectations when the trace and B (typically a scalar multiple of some expression for a free energy) are given is the domain of *statistical mechanics*. However, much of the qualitative theory of statistical mechanics is completely independent of the details involved, and it is this part that we concentrate upon in the following sections.

For later use we prove an upper bound on the expected entropy of an ensemble in terms of the expectation of some Hermitean quantity. In the following result, unlike in Theorem 3.3, S and B are completely unrelated. But the inequality is the better the closer the ensemble matches that considered in Theorem 3.3, and is an equality when the two ensembles agree.

PROPOSITION 3.5. *Let $\langle \cdot \rangle$ be an ensemble with entropy S . Then, for every Hermitean quantity B such that*

$$(27) \quad Z := \text{tr } e^{-B} < \infty,$$

the expected entropy satisfies the inequality

$$(28) \quad \langle S \rangle \leq \mathfrak{k}(\langle B \rangle + \log Z).$$

Equality holds if and only if

$$(29) \quad S = \mathfrak{k}(B + \log Z).$$

PROOF. The equality case suggests to consider the quantity

$$(30) \quad L := B + \log Z - S/\mathfrak{k}.$$

Since

$$\langle S \rangle = \langle \mathfrak{k}(B + \log Z - L) \rangle = \mathfrak{k}(\langle B \rangle + \log Z - \langle L \rangle),$$

(28) follows if we can show that $\langle L \rangle \geq 0$. For this we give two proofs; the first one is more intuitive but assumes commutativity.

(i) If S and L commute then

$$\begin{aligned}\langle e^{-L} \rangle &= \operatorname{tr} (e^{-S/\hbar} e^{-L}) = \operatorname{tr} e^{-S/\hbar - L} \\ &= \operatorname{tr} e^{-B - \log Z} = \operatorname{tr} e^{-B} / Z = 1.\end{aligned}$$

Since $e^{-\alpha} + \alpha - 1 \geq 0$ for all $\alpha \in \mathbb{R}$, Corollary 9.4 of the appendix applies and yields

$$0 \leq \langle e^{-L} + L - 1 \rangle = \langle e^{-L} \rangle + \langle L \rangle - 1 = \langle L \rangle.$$

(ii) For the general case we put $A := B + \log Z$ and $C := -S/\hbar$. Then $\operatorname{tr} e^{-A} = \operatorname{tr} e^{-B} / Z = 1$, whence

$$\begin{aligned}\langle L \rangle &= \langle A + C \rangle = 1 + \langle A - 1 + C \rangle \\ &= \operatorname{tr} e^{-A} + \operatorname{tr} e^{-S/\hbar} (A - 1 + C) \\ &= \operatorname{tr} (1 \cdot e^{-A} + e^C \cdot (A - 1) + e^C C \cdot 1) \geq 0\end{aligned}$$

by Klein's inequality (Proposition 9.3 of the appendix), since

$$1 \cdot e^{-\alpha} + e^\gamma \cdot (\alpha - 1) + e^\gamma \gamma \cdot 1 = e^\gamma (e^{-(\alpha+\gamma)} + (\alpha + \gamma - 1)) \geq 0$$

for all $\alpha, \gamma \in \mathbb{R}$.

□

4. The first law

We now restrict our attention to a small but very important class of ensembles, those describing equilibrium states.

In equilibrium thermodynamics, one distinguishes between extensive and intensive variables. *Extensive variables* depend on the size of the system, and behave additively when a system is split into disjoint subsystems. *Intensive variables* are constant throughout the system, and hence not affected by splitting. This is sometimes referred to as the *0th law of thermodynamics*; it allows one to measure intensive variables – like temperature – by bringing a calibrated instrument that is sensitive to this variable – a thermometer – into equilibrium with the system to be measured.

We therefore model intensive variables by real numbers (which behave like parameters) and extensive variables by Hermitean quantities.

The set of extensive variables depends on the application and on the desired accuracy of the model; it should be chosen in such a way that knowing the measured values of the extensive variables implies (to the accuracy specified) complete knowledge of the state of a thermodynamic system in equilibrium (cf. Remark 5.1(ii) below). Thus the choice of extensive variables is determined by the experimenter. The theory must describe the remaining freedom available to characterize a particular thermodynamic system with this set of extensive variables, and it must describe how the numerical values of interest can be computed for each state of each thermodynamic system.

A basic extensive quantity present in each thermodynamic system is the *internal energy* H ; in addition, there are further basic extensive quantities which we call $a_j (j \in J)$ and collect in a vector a , indexed by J . For the case of *chemical systems* which we treat in a little more detail, we have

$$(31) \quad a_0 = V, \quad a_j = N_j \quad (j \neq 0),$$

where V denotes the *volume* of the system, and each N_j denotes the number of molecules of a fixed chemical composition (we shall say: *particles of species* j).

In the context of statistical mechanics, the expectation algebra is an algebra of functions (for classical physics) or operators (for quantum physics), and H is a particular function or operator called the *Hamiltonian*; specifying the precise form of the Hamiltonian is essentially equivalent to specifying the system under consideration. V is often treated as a real number, whereas, especially for quantum

systems, the particle number operators N_j again have a more involved form. However, for qualitative theory, there is no need to know details about H or N_j ; it suffices to treat them as primitive objects.

It is intuitively clear from the definition of extensive variables that the only functions of independent extensive variables that are again extensive can be linear combinations, and it is a little surprising that the whole machinery of equilibrium thermodynamics follows essentially from the simple assumption that in equilibrium states the entropy is extensive. We formalize this assumption in a slightly more demanding definition.

4.1. Definition.

- (i) A *thermodynamic system* is defined by a choice of Hermitean extensive variables H, a_0, \dots, a_s from an expectation algebra.
- (ii) An *equilibrium state* of the system is an ensemble whose entropy S is a linear combination of the basic extensive quantities of the form

$$(32) \quad S = T^{-1} \left(H - \sum_{j \in J} g_j a_j \right)$$

with suitable real numbers $T \neq 0$ and $g_j (j \in J)$.

In particular, T and g fully characterize an equilibrium state of a given system. (There are, of course, also many nonequilibrium states!) The numbers g_j are called the intensive variables *conjugate to* a_j , and the number T , called the *temperature*, is considered as conjugate to the entropy S , because of the analogy visible by writing (32) in the form

$$(33) \quad H = TS + g \cdot a,$$

called the *Euler equation*. Here g is the vector with components $g_j (j \in J)$.

As the terminology suggests, equilibrium ensembles are good models for physical systems in equilibrium, i.e., systems that do not change macroscopically with time.

Note that an arbitrary linear combination

$$(34) \quad S = \alpha H + h_0 a_0 + \dots + h_s a_s$$

can be written in the form (32) with $T = 1/\alpha$ and $g_j = -h_j/\alpha$, provided that $\alpha \neq 0$; and indeed, (34) is the mathematically more natural form, which also

allows states of infinite temperature excluded in (32). However, the formulation as (32) is unalterably fixed by tradition, so we shall use it here, too. (Incidentally, this shows that negative temperature must be considered to be “higher” than any positive temperature, cf. Landau & Lifschitz [14].)

Note that T and g vary with the state and the entropy depends on them via (32); hence expectations also depend on the particular state a system is in. It is crucial to distinguish between the quantities H and a_j (which are independent of T and g and hence depend on the system but not on the state) and their expectations $\overline{H} = \langle H \rangle$ and $\overline{a}_j = \langle a_j \rangle$ (which change when the state of the system changes).

For chemical systems (31),

$$(35) \quad P := -g_0 \quad \text{and} \quad \mu_j := g_j \quad (j \neq 0)$$

are identified with *pressure* and *chemical potential* (of species j), respectively.

At the moment, temperature, pressure and chemical potential are just names for the intensive variables; that these indeed correspond to physical intuition will follow from the first law.

For a chemical system, we shall always assume that $T > 0$, $P > 0$; the Euler equation takes the form

$$(36) \quad H = TS - PV + \mu \cdot N.$$

One sees that the Euler equation (36) splits the internal energy H into a sum of contributions from different origins, the *thermal energy* (or *heat*) TS , the *mechanical energy* $-PV$, and the *chemical energy* $\mu \cdot N$ which can be split further into the sum of the contributions $\mu_j N_j$ of each species.

For more general thermodynamic systems, Table 4.1 displays some typical extensive variables, their intensive conjugate variables, and their contribution to the internal energy. Some of the extensive variables (and their conjugates) are vectors themselves.

extensive a_j	intensive g_j	energy contribution $g_j a_j$
length L	tension J	JL , mechanical
surface A	surface tension σ	σA , mechanical
volume V	pressure $-P$	$-PV$, mechanical
Polarization P	electr. field strenght E	$E \cdot P$, electrical
magnetization M	magn. field strenght B	$B \cdot M$, magnetical
particle number N_j	chem. potential μ_j	$\mu_j N_j$, chemical
entropy S	temperature T	TS , thermal

Table 4.1 . Typical conjugate pairs of thermodynamic variables.

The Hamiltonian H plays a very distinguished role in the dynamics of physical systems. This can not yet be seen in our present static treatment, but one feature distinguishes H from the other extensive variables like S, V, N_j (and from the intensive variables T, P, μ_j) even at equilibrium: The expectations $\overline{S}, \overline{V}, \overline{N}_j$ (and the numbers T, P, μ_j) can be directly controlled macroscopically by a proper arrangement of the boundary conditions; but the expected internal energy \overline{H} is solely governed by the microscopic dynamics and can be controlled only indirectly via the equation of state.

From the requirement that the entropy defines an ensemble, $1 = \langle 1 \rangle = \text{tr } e^{-S/\kappa}$, and we find as immediate consequence:

PROPOSITION 4.1. *The intensive variables are related by the equation*

$$(37) \quad \text{tr } e^{-\beta(H-g \cdot a)} = 1,$$

where

$$(38) \quad \beta = \frac{1}{\kappa T} \quad . \quad \square$$

As explained before, the *coldness* β defined by (38) is a more natural variable than the temperature T , and figures prominently in statistical mechanics. In the limit $T \rightarrow 0$, a system becomes infinitely cold, giving a nice intuition for the unattainability of zero absolute temperature. (Cf. the remarks after Definition 6.3.)

Equation (37), and any equivalent equation is called an *equation of state* of the system. It relates the intensive variables β (or T) and g . The set of pairs (H, g) for which the trace in (37) is defined and has the value 1 is called the *state space* of the

thermodynamic system. The equation of state shows that, apart from singularities describing so-called *phase transitions*, the state space has the structure of an s -dimensional manifold in \mathbb{R}^{s+1} , where s is the number of intensive variables other than the temperature. In *phenomenological thermodynamics* one makes suitable, more or less heuristic assumptions on the form of this manifold.

In thermodynamic models for *dilute gases*, the volume V is represented in the expectation algebra as a real number. Equation (37) can then be rewritten as

$$\begin{aligned} 1 &= \operatorname{tr} e^{-\beta(H+PV-\mu\cdot N)} = e^{-\beta PV} \operatorname{tr} e^{-\beta(H-\mu\cdot N)}, \\ e^{\beta PV} &= \operatorname{tr} e^{-\beta(H-\mu\cdot N)}; \end{aligned}$$

taking logarithms and multiplying with $\beta^{-1} = kT$, we find an equation of state of the form

$$(39) \quad PV = kT \log Z(T, \mu),$$

where

$$(40) \quad Z(T, \mu) := \operatorname{tr} e^{-\beta(H-\mu\cdot N)}$$

is the so-called *partition function* of the system.

COROLLARY 4.2. *For a dilute gas, expectations of a quantity A are calculated from (38) and*

$$(41) \quad \langle A \rangle = \frac{1}{Z(T, \mu)} \operatorname{tr} \left(A e^{-\beta(H-\mu\cdot N)} \right).$$

PROOF.

$$\begin{aligned} \langle A \rangle &= \operatorname{tr} \left(A e^{-S/k} \right) = \operatorname{tr} \left(A e^{-\beta(H+PV-\mu\cdot N)} \right) \\ &= e^{-\beta PV} \operatorname{tr} \left(A e^{-\beta(H-\mu\cdot N)} \right) = \frac{1}{Z(T, \mu)} \operatorname{tr} \left(A e^{-\beta(H-\mu\cdot N)} \right) \end{aligned}$$

by (39). \square

At a phase transition, the assumption to treat V as a real number is no longer justified, since near phase transitions, PV is a multivalued function of T and μ , in contrast to the conclusion (39).

4.2. Remark. In microscopic calculations of statistical mechanics (see e.g. Gibbs [6], Huang [10]), Reichl [19], the ensemble corresponding to (36), (39) is called a *grand canonical ensemble*, and the negative of (39) is called the *grand potential*. This grand potential also depends on the integration volume V until the so-called thermodynamic limit is performed which suppresses all terms growing slower than $O(V)$. This slight difference to the present reasoning finds its explanation in the fact that a microscopic theory yields the additivity of entropy only in the thermodynamic limit (see e.g. Thirring [22]), while our macroscopic treatment *assumes* this from the start.

The advantage we gain is that a much simpler machinery suffices to obtain our results. The price we pay is that, in the present – static – setting, we can only reconstruct *phenomenological* thermodynamics but cannot deduce quantitatively the equation of state from microscopic properties. We also do not get the microscopic interpretation of extensive variables as *conserved quantities* (whence additivity) and of intensive variables as *fields* (which cause non-equilibrium currents when they are not constant). This lack of generality will be corrected in later papers that treat nonequilibrium situations.

To be able to formulate the thermodynamic laws we also need the concept of a reversible change of states, i.e., changes preserving equilibrium. Since in actual practice, reversible changes can be realized only through infinitesimally slow movement, it is appropriate to formalize this as follows.

4.3. Definition.

- (i) A *reversible transformation* is a continuously differentiable mapping

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

from a real interval into the state space.

- (ii) A *state variable* is a function $f(T, g)$ defined on the state space (or a subset).

Note that the differential

$$(42) \quad df = \frac{\partial f}{\partial T} dT + \frac{\partial f}{\partial g} \cdot dg$$

describes the change of a state variable f under arbitrary reversible transformations: divide by $d\lambda$ and recognize the chain rule!

We now obtain the first law of thermodynamics from the observation that, since the entropy depends on T and g only, the expectation of arbitrary quantities form state variables. In particular we may consider changes of the expectations of extensive

variables, which represent predictions for measurements of these variables. This gives *phenomenological* statements, i.e., statements relating expectations (and not quantities) that can be compared with experiments.

THEOREM 4.3.

(i) *For every equilibrium state we have the phenomenological Euler equation*

$$(43) \quad \begin{aligned} \overline{H} &= T\overline{S} + g \cdot \overline{a} \\ & (= T\overline{S} - P\overline{V} + \mu \cdot \overline{N} \text{ for chemical systems}). \end{aligned}$$

(ii) *For reversible changes we have the first law of thermodynamics*

$$(44) \quad \begin{aligned} d\overline{H} &= Td\overline{S} + g \cdot d\overline{a} \\ & (= Td\overline{S} - Pd\overline{V} + \mu \cdot d\overline{N} \text{ for chemical systems}). \end{aligned}$$

and the Gibbs-Duhem equation

$$(45) \quad \begin{aligned} 0 &= \overline{S}dT + \overline{a} \cdot dg \\ & (= \overline{S}dT - \overline{V}dP + \overline{N} \cdot d\mu \text{ for chemical systems}). \end{aligned}$$

PROOF. We take expectations in (33), and note that T and g are real numbers; then (43) follows. Since H and a are fixed quantities for a given system, they do not change under reversible transformations. This is a crucial fact, since it allows us to obtain the relation

$$(46) \quad 0 = TdS + SdT + a \cdot dg$$

by differentiating (33). Since, by Corollary A.2 of the appendix, ■

$$(47) \quad \langle dS \rangle = \text{tr} \left(e^{-S/\kappa} dS \right) = \text{tr} \left(\kappa d(e^{-S/\kappa}) \right) = \kappa d \left(\text{tr} e^{-S/\kappa} \right) = \kappa(d1) = 0,$$

taking expectations in (46) implies the Gibbs-Duhem equation. Finally, if we differentiate (43), we obtain

$$d\overline{H} = Td\overline{S} + \overline{S}dT + g \cdot d\overline{a} + \overline{a} \cdot dg,$$

and using (45), this simplifies to the first law of thermodynamics. \square

4.4. Remarks. The following discussion fills our so far purely mathematical development with physical meaning.

- (i) If we write $U = \overline{H}$ for the expected internal energy and drop the bars in $\overline{S}, \overline{V}, \overline{N}$, these are just the classical relations of equilibrium thermodynamics.
- (ii) Equation (44), the first law of thermodynamics, describes the external (“macroscopic”) balance of the energy in a reversible process. In chemical systems, the total energy $d\overline{H}$ flowing into the system is composed of the *heat flux* $Td\overline{S}$ (usually written dQ , the bar indicating that this is an inexact 1-form and not a differential), the *mechanical energy flux* $-Pd\overline{V}$ and the *chemical energy flux* $\mu \cdot d\overline{N}$. The interpretation of $-Pd\overline{V}$ as mechanical energy flux also shows that the intensive variable P was indeed correctly identified as pressure, and a similar argument shows that the name chemical potential for μ is indeed appropriate.
- (iii) In case of thermal, mechanical or chemical isolation, \overline{S} , \overline{V} , or \overline{N} must remain constant, respectively, and the corresponding fluxes vanish, consistent with our intuition. Because of the form of the energy terms in (44), one often uses the analogy to mechanics and calls the intensive variables *generalized forces*, and differentials of extensive variables *generalized displacements*.
- (iv) If we write the first law in the form

$$Td\overline{S} = d\overline{H} + Pd\overline{V} - \mu \cdot d\overline{N}$$

we get the traditional definition of temperature (or rather the inverse coldness) as an integrating factor of this 1-form, and of the entropy as the corresponding integral

$$\overline{S} = \int \frac{1}{T}(d\overline{H} + Pd\overline{V} - \mu \cdot d\overline{N}).$$

The *existence* of the integrating factor and hence of entropy is traditionally deduced from an analysis of the Carnot cycle, taking the impossibility of perpetual motion as an experimental fact. In our development, this impossibility would appear rather as a consequence of our assumptions.

- (v) Equation (45), the Gibbs-Duhem equation, describes the internal (“microscopic”) energy balance necessary to compensate the changes $d(T\overline{S}) = Td\overline{S} + \overline{S}dT$ of thermal energy, $d(P\overline{V}) = Pd\overline{V} + \overline{V}dP$ of mechanical energy, and $d(\mu \cdot \overline{N}) = \mu \cdot d\overline{N} + \overline{N} \cdot d\mu$ of chemical energy.
- (vi) (45) implies that for chemical systems at constant T, μ , the pressure P cannot change infinitesimally; hence P can take only a limited number of values for given T, μ , corresponding to the various *phases* of the system.

Thus, for a fixed phase (and hence usually only in a subset of the state space), we can write P as a continuously differentiable function of T and μ ,

$$(48) \quad P = P(T, \mu).$$

This is a form of the equation of state, and generalizes equation (39) valid for dilute gases only.

COROLLARY 4.4. *For a chemical system in equilibrium, the expectations of the extensive quantities are given by*

$$(49) \quad \bar{S} = V \frac{\partial P(T, \mu)}{\partial T}, \quad \bar{N}_j = V \frac{\partial P(T, \mu)}{\partial \mu_j},$$

$$(50) \quad \bar{H} = V \left(-P + T \frac{\partial P(T, \mu)}{\partial T} + \mu \cdot \frac{\partial P(T, \mu)}{\partial \mu} \right).$$

PROOF. Consider the reversible transformation obtained by keeping all intensive variables except T or μ_j fixed, and divide the Gibbs-Duhem equation (45) by dT or $d\mu_j$, respectively. This gives (49), and (50) then follows from the Euler equation (43). \square

Thus everything of macroscopic interest is deducible from the equation of state, and this explains why, in many situations, one can use thermodynamics very successfully as a phenomenological theory without having to bother about microscopic details.

In practice it may be more profitable to solve equation (49) or (50) for some of the variables T, μ_j , and substitute these into the other equations. In particular, for a pure substance (only one chemical species), all extensive and intensive variables (or rather their expectations) can be expressed in terms of any non-conjugate pair of them. The relations (43)–(45) can then be used as in the previous proof to give simple formulas for the other variables. (This is the most convenient way to organize the wealth of thermodynamic relations obtained by fixing two arbitrary variables, and it easily extends to more general situations.)

5. The second law

We now discuss the concept of entropy, defined in Section 3 and related to physics in Section 4, in the light of our introductory example in Section 1. The extent to which the analogy between this example and the general case is valid will be discussed later, since it is related to the third laws of thermodynamics. For the moment we shall simply assume that it is justified to consider the *expected entropy*

$$(51) \quad \bar{S} = \text{tr} (S\rho) = -k \text{tr} (\rho \log \rho)$$

(by Proposition 3.4) as a measure of *expected information deficit*; cf (10). Thus, measured in the right units, the expected entropy equals the expected number of optimal decisions (yes–no questions) needed to completely specify a (microscopic) situation of which we know only (macroscopic) expectations.

In this way, entropy quantifies the *intrinsic* (microscopic) *complexity* present in any system modelled by a (macroscopic) thermodynamic state. Note that the equilibrium states described by classical thermodynamics are macroscopically highly uniform; their intrinsic complexity is apparent only in a microscopic treatment, and the only macroscopic shadow of this complexity is the expected entropy and the associated heat (apart from fluctuations which become macroscopically relevant only in special circumstances; see Section 8). In particular, the traditional interpretation of entropy as a measure of disorder is often misleading: *macroscopic disorder* is not measured by entropy but by the *absence of macroscopic space and time correlations*, and in this sense, equilibrium states are the most ordered macroscopic states in the universe, and not the most disordered ones, as tradition suggests. If you pour milk into your coffee, stirring mixes coffee and milk thus increasing complexity; but macroscopic order is restored after some time when this increased complexity has become macroscopically inaccessible (in a state of maximal entropy, as we shall see in a moment).

A system not in equilibrium is characterized by local (macroscopic) inhomogeneities (like the filaments of milk still visible for a while), indicating that the (constant) expectations of the extensive variables alone do not exhaust all available macroscopic information. This extra macroscopic information of course reduces the intrinsic complexity remaining, and if our interpretation of entropy as intrinsic complexity is appropriate, this should be a consequence of our theory: The equilibrium state should be a state without additional macroscopic information and hence with maximal expected entropy. Indeed, this is the contents of the second law of thermodynamics in its most general form. Expressed succinctly, at equilibrium, *macroscopic order* (homogeneity) is perfect and *microscopic complexity* is

maximal (perfect mixing).

THEOREM 5.1. (*Second law of thermodynamics*)

If S is the entropy of an arbitrary ensemble $\langle \cdot \rangle$ with the same expectations

$$(52) \quad \langle H \rangle = \langle H \rangle_{eq}, \quad \langle a \rangle = \langle a \rangle_{eq}$$

as an equilibrium ensemble $\langle \cdot \rangle_{eq}$ with entropy S_{eq} then

$$(53) \quad \langle S_{eq} \rangle_{eq} = \langle S_{eq} \rangle \geq \langle S \rangle.$$

Equality only holds if $S = S_{eq}$.

PROOF. We apply Proposition 3.5 with $B = S_{eq}/\mathfrak{k}$. For this choice,

$$Z = \text{tr } e^{-B} = \langle 1 \rangle_{eq} = 1.$$

If T and g denote the intensive variables of the equilibrium ensemble then $S_{eq} = T^{-1}(H - g \cdot a)$, whence

$$\begin{aligned} \langle S \rangle &\leq \mathfrak{k}(\langle B \rangle + \log Z) = \langle S_{eq} \rangle = \langle T^{-1}(H - g \cdot a) \rangle \\ &= T^{-1}(\langle H \rangle - g \cdot \langle a \rangle) = T^{-1}(\langle H \rangle_{eq} - g \cdot \langle a \rangle_{eq}) \\ &= \langle T^{-1}(H - g \cdot a) \rangle_{eq} = \langle S_{eq} \rangle_{eq}. \end{aligned}$$

□

5.1. Remarks.

- (i) If $T > 0$ and $g \geq 0$ then one finds in the same way that (53) holds already under the weaker assumptions

$$\langle H \rangle \leq \langle H \rangle_{eq}, \quad \langle a \rangle \geq \langle a \rangle_{eq},$$

and similar statements hold if $T > 0$ and only some components of g have fixed sign. In particular, for a chemical system, where $T > 0$ and $g_0 = -P < 0$, (53) holds whenever

$$(54) \quad \langle H \rangle \leq \langle H \rangle_{eq}, \quad \langle V \rangle \leq \langle V \rangle_{eq}, \quad \langle N \rangle = \langle N \rangle_{eq}.$$

If we take for $\langle \cdot \rangle$ another equilibrium ensemble we conclude that at fixed expected particle number, the expected entropy increases when \overline{H} or \overline{V} (or both) increase reversibly. (This also follows from (59) below.)

- (ii) The equilibrium ensemble is uniquely determined by the expectations \overline{H} and \overline{a} . Indeed, if S_{eq} and S'_{eq} are equilibrium entropies then Theorem 5.1 applied twice gives

$$\langle S'_{eq} \rangle'_{eq} \geq \langle S_{eq} \rangle_{eq} \geq \langle S'_{eq} \rangle'_{eq}.$$

Hence the expected entropy is the same, and again by Theorem 5.1, the entropies themselves and hence the ensembles agree.

- (iii) The difference

$$(55) \quad \overline{S}_{eq} - \overline{S} = \langle S_{eq} - S \rangle = \langle S_{eq} \rangle_{eq} - \langle S \rangle \geq 0,$$

known as *relative entropy* (Thirring [22], 2.2.22), can be interpreted as the expected amount of macroscopic information in an ensemble $\langle \cdot \rangle$ which cannot be explained by the knowledge of \overline{H} and \overline{a} only. This interpretation makes sense since the relative entropy vanishes at equilibrium and by (ii), all equilibrium expectations are completely determined by \overline{H} and \overline{a} , so that an equilibrium ensemble carries no information not already contained in \overline{H} and \overline{a} (and, of course, the equation of state). A large relative entropy therefore indicates that some important macroscopic quantity or quantities were neglected in the list of extensive variables.

- (iv) To our present knowledge and assuming proper modelling, all spontaneous changes in nature decrease the relative entropy and hence the macroscopically accessible unexplained information. A change of state with this property, i.e.

$$(56) \quad d\overline{S}_{eq} - d\overline{S} = d(\langle S_{eq} \rangle_{eq} - \langle S \rangle) < 0$$

(interpreted as an inequality after integration over a path in state space) is called *irreversible*; the difference (56) is called the associated *entropy production*. Under natural conditions, irreversibility of changes in time and asymptotic attainment of equilibrium can be derived from rather general dynamical assumptions; this will be discussed in a subsequent paper. Without dynamics, we can only assert the much weaker inequality (53).

While the relative entropy may decrease spontaneously, the expected entropy itself may increase or decrease depending on the circumstances. For

example, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ may happen spontaneously (under suitable conditions) though it decreases the entropy (e.g. at constant $T = 25^\circ \text{ C}$ and $P = 1 \text{ atm}$). The only situation where the expected entropy must increase in spontaneous changes is when \overline{H} and \overline{a} (thus for a chemical system $\overline{H}, \overline{V}, \overline{N}$) are kept constant. However, such conditions are not realized in nature, not even for the universe as a whole (which expands, i.e. \overline{V} changes). Thus, while the second law in the form of a maximum entropy principle is of great theoretical importance, it is not the extremum principle ruling nature. Indeed, the irreversible nature of the second law is usually manifest as *friction*, i.e. *energy dissipation*, irrespective of the entropy balance, and the relevant extrema principles are those of minimal free energy.

In order to discuss these principles we need to extend the definition of intensive variables, so far only defined for equilibrium ensembles as coefficients in the Euler equation, to arbitrary ensembles. However this poses some problems since the Euler equation defines equilibrium states and hence cannot be used for nonequilibrium situations. However, the Euler equation for the expectations can be made a starting point, and if there is at least one pair (T, g) belonging to the state space of the thermodynamic system such that

$$(57) \quad \langle H \rangle = \langle TS + g \cdot a \rangle,$$

we call $\langle \cdot \rangle$ a *thermodynamic ensemble* with intensive variables T, g, λ , (not necessarily uniquely determined by the ensemble). We can now rephrase the second law of thermodynamics as follows:

THEOREM 5.2. *Let $\langle \cdot \rangle_\lambda$ be a family of thermodynamic ensembles with fixed expectations*

$$(58) \quad \langle H \rangle_\lambda = \overline{H} \text{ and } \langle a \rangle_\lambda = \overline{a}$$

and entropies

$$(59) \quad \langle S \rangle_\lambda = \overline{S}(\lambda) = T(\lambda)^{-1}(\overline{H} - g(\lambda) \cdot \overline{a}).$$

Then the equilibrium ensemble with the same expectations \overline{H} and \overline{a} satisfies

$$(60) \quad \langle S_{eq} \rangle_{eq} \geq \sup_\lambda \overline{S}(\lambda).$$

Moreover, for irreversible changes at fixed \overline{H} and \overline{a} ,

$$(61) \quad d\overline{S}(\lambda) > 0,$$

i.e. the expected entropy increases.

(Attainment of the supremum cannot be derived without making dynamical assumptions.)

PROOF. (59) follows directly from (57), (60) from (53), and (61) follows from (56) since at fixed \overline{H} and \overline{a} the equilibrium ensemble is fixed so that $d\langle S_{eq} \rangle_{eq} = 0$. \square

Since the assumptions of constant \overline{H} , \overline{a} are unrealistic, we want to derive similar extremality results under more realistic boundary conditions. For chemical systems, it is possible to prepare the states in such a way that one of the following sets of variables is kept approximately fixed:

- (i) \overline{S} , \overline{V} and \overline{N} (isolated, closed vessel),
- (ii) T , \overline{V} and \overline{N} (closed vessel in a heat bath),
- (iii) \overline{S} , P and \overline{N} (isolated, open vessel),
- (iv) T , P and \overline{N} (open vessel in a heat bath);

in cases (ii)–(iv), T is the temperature of the heat bath and P the pressure of the surrounding. (It is also possible to fix $\overline{\mu}$ by using a chemical bath, with similar consequences as in the above cases.) In the first case, a strong assertion can be made.

THEOREM 5.3. (*Energy dissipation*)

For any irreversible process at constant \overline{S} and \overline{a} (i.e., for chemical systems, at constant $\overline{S}, \overline{V}, \overline{N}$), the internal energy

$$(62) \quad U := \overline{H}$$

is strictly decreasing, and has at equilibrium a minimum that belongs to a stationary point.

PROOF. At equilibrium, the first law of thermodynamics holds and gives

$$d\overline{H} = d\langle H \rangle_{eq} = T_{eq} d\langle S_{eq} \rangle_{eq} + g_{eq} \cdot d\langle a \rangle_{eq},$$

hence

$$(63) \quad d\bar{H} = T_{eq} d\bar{S} + g_{eq} \cdot d\bar{a} - \Delta$$

with

$$(64) \quad \Delta := T_{eq} (d\bar{S} - d\langle S_{eq} \rangle_{eq}) > 0.$$

Here we assumed $T_{eq} > 0$. If \bar{S} and \bar{a} are kept constant then $d\bar{S} = d\bar{a} = 0$, hence

$$(65) \quad d\bar{H} = -\Delta < 0,$$

i.e. $U = \bar{H}$ is strictly decreasing. As equilibrium is approached, $\Delta \rightarrow 0$ hence $d\bar{H} \rightarrow 0$, and we find a stationary point at equilibrium, which clearly is a minimizer. \square

(64) and (65) express the fact that energy is lost or *dissipated*, i.e., becomes macroscopically unavailable, and the energy dissipation is proportional to the entropy production. (63) and (64) are often combined to the *first and second law*

$$d\bar{H} \leq T d\bar{S} + g \cdot d\bar{a}$$

$$(d\bar{H} \leq d\bar{S} - Pd\bar{V} + \mu \cdot dN \text{ for chemical systems}),$$

but this formulation conceals the difference between equilibrium and nonequilibrium intensive quantities, a common practice in treatises of thermodynamics and statistical physics.

In the other cases, it seems impossible to make general assertions far from equilibrium, and we are only able to prove weaker statements. This has to do with the fact that in general $T_{eq} \neq T$, etc.: For example, keeping T_{eq} , \bar{V} and \bar{N} fixed, say, would imply, by relations valid at equilibrium, that \bar{S} , \bar{V} and \bar{N} are fixed, which does not describe the intended situation (ii). Typical textbooks simply ignore this problem, proceed as if $T_{eq} = T$ etc., and hence “derive” stronger results comparable with Theorem 5.3.

THEOREM 5.4. (*Variational principles for free energies*)

- (i) For any irreversible process at constant T and \bar{a} (i.e., for chemical systems, T , \bar{V} and \bar{N}), the Helmholtz free energy

$$(66) \quad A := \bar{H} - T\bar{S}$$

has at equilibrium a stationary point.

- (ii) For any irreversible chemical process at constant \bar{S} , P and \bar{N} , the enthalpy

$$(67) \quad H_{ent} := \bar{H} + P\bar{V}$$

has at equilibrium a stationary point.

- (iii) For any irreversible chemical process at constant T , P and \bar{N} , the Gibbs free energy

$$(68) \quad G := \mu \cdot \bar{N} = A + P\bar{V}$$

has at equilibrium a stationary point.

(Usually, these stationary points are local minimizers.)

PROOF. In case (i), $d\bar{a} = 0$ and $dT = 0$, so that

$$dA = d(\bar{H} - T\bar{S}) = d\bar{H} - Td\bar{S} = (T_{eq} - T) d\bar{S} \rightarrow 0$$

as equilibrium is approached.

In the other cases, $dP = 0$, $d\bar{N} = 0$, hence (63) gives

$$(69) \quad d\bar{H} = T_{eq} d\bar{S} - P_{eq} d\bar{V} - \Delta$$

Now in case (ii), $d\bar{S} = 0$, hence

$$dH_{ent} = d\bar{H} + Pd\bar{V} = (P - P_{eq}) d\bar{V} - \Delta \rightarrow 0$$

as equilibrium is approached. And in case (iii), $dT = 0$, hence

$$dG = d\bar{H} - Td\bar{S} + Pd\bar{V} = (T_{eq} - T) d\bar{S} + (P - P_{eq}) d\bar{V} - \Delta \rightarrow 0$$

as equilibrium is approached. \square

The difference terms are *second order* hence usually (if entropy production is large enough) they can be neglected, and show that locally, the free energies (66--68) are indeed local minima. (But this sounds now cryptic to me.)

try to be stronger (without irreversibility, just use a family of ensembles containing a stationary point). If so, case (i) is also interesting again.

Then discuss phases and metastability, etc.

6. Third law and quantization

The third law of thermodynamics asserts that the expected entropy is always nonnegative. Of course, this is a necessary requirement for the interpretation of expected entropy as expected optimal number of questions, but it cannot be deduced from our axioms without making further assumptions, as a simple example demonstrates.

6.1. Example: The algebra E of vectors of length m with pointwise operations becomes an expectation algebra for any trace of the form

$$\text{tr } A = \frac{1}{m} \sum_{i=1}^m t_i A_i \quad (t_i > 0);$$

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

$$\langle A \rangle = \frac{1}{m} \sum_{i=1}^m A_i,$$

is an ensemble with

$$\rho_i = \frac{1}{t_i}, \quad S_i = k \log t_i$$

and expected entropy

$$\bar{S} = \frac{1}{m} \sum_{i=1}^m S_i = \frac{k}{m} \log \left(\prod_{i=1}^m t_i \right),$$

which is negative if we choose the t_i such that $\prod_i t_i < 1$.

Thus we need an extra condition which brings us closer to the situation discussed in Section 1. There the trace was a sum over the components, and since functions were defined componentwise,

$$(70) \quad \text{tr } f(A) = \sum_{n \in \mathcal{N}} f(A_n).$$

6.2. Definition. A Hermitean quantity A is called *quantized* if $\text{tr } A$ exists and there is a countable family A_n ($n \in \mathcal{N}$) of real numbers such that (70) holds for every function f for which the right hand side is absolutely convergent. The numbers A_n are called the *levels* of A .

According to our definition, quantization has nothing to do with microscopic properties; indeed, for the counter discussed in Section 1, *all* Hermitean quantities are quantized. Quantization is the key to the third law:

THEOREM 6.1. (Third law of thermodynamics)

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

PROOF. We have

$$(71) \quad 1 = \text{tr } \rho = \text{tr } e^{-S/k} = \sum_{n \in \mathcal{N}} e^{-S_n/k} = \sum_{n \in \mathcal{N}} \rho_n \quad ,$$

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

$$(72) \quad \bar{S} = \text{tr } S\rho = \text{tr } S e^{-S/k} = \sum_{n \in \mathcal{N}} S_n e^{-S_n/k} = \sum_{n \in \mathcal{N}} S_n \rho_n.$$

If $\mathcal{N} = \{n\}$ then (71) implies $\rho_n = 1$, $S_n = 0$, and (72) gives $\bar{S} = 0$. And if $|\mathcal{N}| > 1$ then (71) gives $\rho_n < 1$, hence $S_n > 0$ for all $n \in \mathcal{N}$, and (72) implies $\bar{S} > 0$. \square

To get further insight into quantization, we must extend the definition a little to functions involving several quantities.

6.3. Definition.

- (i) A family $A^{(1)}, \dots, A^{(s)}$ of pairwise commuting Hermitean quantities is called *quantized* if $\text{tr } A^{(1)}, \dots, \text{tr } A^{(s)}$ exists and there is a countable family $(A_n^{(1)}, \dots, A_n^{(s)})$ ($n \in \mathcal{N}$) of real vectors such that

$$(73) \quad \text{tr } f(A^{(1)}, \dots, A^{(s)}) = \sum_{n \in \mathcal{N}} f(A_n^{(1)}, \dots, A_n^{(s)})$$

for all functions f for which the right hand side is absolutely convergent. The set

$$(74) \quad \Sigma = \{(A_n^{(1)}, \dots, A_n^{(s)}) \mid n \in \mathcal{N}\}$$

is called the *joint spectrum* of $A^{(1)}, \dots, A^{(s)}$. The joint spectrum is called *degenerate* if some of the vectors $(A_n^{(1)}, \dots, A_n^{(s)})$ are identical, and *nondegenerate* otherwise.

- (ii) A family $A^{(1)}, \dots, A^{(s)}$ of pairwise commuting Hermitean quantities is called *maximal* if every quantity commuting with $A^{(1)}, \dots, A^{(s)}$ can be written as a function of $A^{(1)}, \dots, A^{(s)}$. (This is a natural definition since any function of $A^{(1)}, \dots, A^{(s)}$ commutes with $A^{(1)}, \dots, A^{(s)}$.)

In quantum chemistry, energy H , volume V and particle numbers N_1, \dots, N_s form a quantized family of pairwise commuting Hermitean variables. As a consequence, the entropy $S = T^{-1}(H + PV - \mu \cdot N)$ is quantized, too, so that the third law of thermodynamics is valid. The number of levels is infinite, so that the expected entropy is positive. Zero expected entropy is therefore an idealization which cannot be realized in practice. But in this idealized situation, Theorem 6.1 implies that entropy and hence the joint spectrum of (H, V, N_1, \dots, N_s) can have a single level only. This is the situation discussed in ordinary quantum mechanics (pure energy states at fixed particle numbers). It is usually associated with the limit $T \rightarrow 0$, though at absolute temperature $T = 0$, i.e., infinite coldness, the thermodynamic formalism fails (but low T asymptotic expansions are possible).

6.4. Convention. In the following, $A^{(1)}, \dots, A^{(s)}$ always denotes a quantized family of pairwise commuting Hermitean quantities with joint spectrum (74). \mathcal{N}_0 denotes a subset of \mathcal{N} such that the $(A_n^{(1)}, \dots, A_n^{(s)})(n \in \mathcal{N}_0)$ enumerate the joint spectrum without repetition; thus $\mathcal{N}_0 = \mathcal{N}$ iff the joint spectrum is nondegenerate.

PROPOSITION 6.2.

$$f(A^{(1)}, \dots, A^{(s)}) = 0 \iff f(A_n^{(1)}, \dots, A_n^{(s)}) = 0 \text{ for all } n \in \mathcal{N}.$$

PROOF. Let $A = f(A^{(1)}, \dots, A^{(s)})$. Then $A^* = f^*(A^{(1)}, \dots, A^{(s)})$ since $A^{(1)}, \dots, A^{(s)}$ are Hermitean. Therefore

$$\begin{aligned} \text{tr } AA^* &= \text{tr } f(A^{(1)}, \dots, A^{(s)}) f^*(A^{(1)}, \dots, A^{(s)}) \\ &= \sum f(A_n^{(1)}, \dots, A_n^{(s)}) f^*(A_n^{(1)}, \dots, A_n^{(s)}) \\ &= \sum |f(A_n^{(1)}, \dots, A_n^{(s)})|^2 \end{aligned}$$

vanishes iff all $f(A_n^{(1)}, \dots, A_n^{(s)}) = 0$. But $\text{tr } AA^* = 0$ is equivalent to $A = 0$. \square

If we apply the proposition to the difference we see that functions of $A^{(1)}, \dots, A^{(s)}$ which agree on the joint spectrum define identical quantities $f(A^{(1)}, \dots, A^{(s)})$. Therefore, values outside the joint spectrum are completely irrelevant, and it is

consistent to interpret this as saying that the joint spectrum gives the set of *possible values* which $A^{(1)}, \dots, A^{(s)}$ can attain *simultaneously*. (The logical details and the problems arising for *noncommuting* quantities are discussed in the next section.)

PROPOSITION 6.3. *There is a family $E_n (n \in \mathcal{N}_0)$ of mutually orthogonal Hermitian idempotents, i.e.,*

$$(75) \quad E_n^2 = E_n = E_n^*,$$

$$(76) \quad E_m E_n = E_n E_m = 0 \quad \text{if } m \neq n,$$

giving the spectral resolution of functions of $A^{(1)}, \dots, A^{(s)}$, i.e.,

$$(77) \quad f(A^{(1)}, \dots, A^{(s)}) = \sum_{n \in \mathcal{N}_0} f(A_n^{(1)}, \dots, A_n^{(s)}) E_n,$$

and in particular

$$(78) \quad A^{(k)} = \sum_{n \in \mathcal{N}_0} A_n^{(k)} E_n \quad \text{for } k = 1, \dots, s.$$

PROOF. For $n \in \mathcal{N}_0$ (cf. the Convention), let f_n be a function such that

$$(79) \quad f_n(A_n^{(1)}, \dots, A_n^{(s)}) = 1, \quad f_n(A_m^{(1)}, \dots, A_m^{(s)}) = 0 \quad \text{for } m \in \mathcal{N}_0 \setminus \{n\},$$

and put

$$(80) \quad E_n := f_n(A^{(1)}, \dots, A^{(s)}).$$

By construction of f_n , the functions f_n^2 , f_n and f_n^* agree on the joint spectrum, whence (75) holds. Similarly, $f_m f_n$ and $f_n f_m$ vanish on the joint spectrum when $m \neq n$, proving (76). Finally, f and $\sum_{n \in \mathcal{N}_0} f(A_n^{(1)}, \dots, A_n^{(s)}) f_n$ agree on the joint spectrum, proving (77), and (78) is a special case of this. \square

COROLLARY 6.4. *The multiplicity with which $(A_n^{(1)}, \dots, A_n^{(s)})$ occurs in the joint spectrum is given by $\text{tr } E_n$. In particular, $\text{tr } E_n$ is a positive integer except possibly when $A_n^{(1)} = \dots = A_n^{(s)} = 0$ where it may be infinity.*

PROOF. The first assertion follows by taking $f = f_n$ in (73) and using (79). If we apply this to (78) we find

$$(81) \quad \text{tr } A^{(k)} = \sum_{n \in \mathcal{N}_0} A_n^{(k)} \text{tr } E_n,$$

and since this must be finite we conclude that $\text{tr } E_n$ is finite unless $A_n^{(k)} = 0$ for all k . As a multiplicity it must be a positive integer. \square

We are now ready to construct a Hilbert space of wave functions, using as our only assumption that, in a sense made precise below, there are enough quantized Hermitean quantities. In all previous treatments of quantum theory, this Hilbert space had to be assumed without justification, or deduced from a quantum logic that itself requires justification. See Jammer [11] for the history of attempts to understand the foundations of quantum mechanics.

THEOREM 6.5. *Let $A^{(1)}, \dots, A^{(s)}$ be a maximal family of pairwise commuting Hermitean quantities that is quantized and has a nondegenerate joint spectrum (74). Then the expectation algebra \mathbb{E} has a faithful representation as an algebra of linear operators on a Hilbert space \mathbb{H} which has an orthonormal basis consisting of eigenfunctions $|n\rangle$ ($n \in \mathcal{N}$) such that*

$$(82) \quad A^{(1)}|n\rangle = A_n^{(1)}|n\rangle, \dots, A^{(s)}|n\rangle = A_n^{(s)}|n\rangle,$$

i.e., the $A_n^{(k)}$ are the eigenvalues of $A^{(k)}$. Moreover,

$$(83) \quad \text{tr } A = \sum_{n \in \mathcal{N}} \langle n|A|n\rangle,$$

and

$$(84) \quad \langle \psi_1|A|\psi_2\rangle^* = \langle \psi_2|A^*|\psi_1\rangle \text{ for all } A \in \mathbb{E}, |\psi_1\rangle, |\psi_2\rangle \in \mathbb{H}.$$

In particular, Hermitean quantities are represented by self-adjoint linear operators on \mathbb{H} .

Here we used the traditional ket notation $|\psi\rangle$ for wave functions, i.e., elements of \mathbb{H} , the bra notation $\langle \psi| = |\psi\rangle^$ for elements of the dual space of bounded linear functionals of \mathbb{H} , and the bra-ket (bracket)*

$$(85) \quad \langle \psi_1 | \psi_2 \rangle = |\psi_1\rangle^* | \psi_2 \rangle$$

denotes the inner product in H . (Therefore, the bracket in (83) is the inner product of $|n\rangle$ and $A|n\rangle$.) If there are only finitely many levels, $\mathcal{N} = \{1, \dots, N\}$ we can take $H = \mathbb{C}^N$; then kets $|\psi\rangle$ are column vectors ψ , bras $\langle\psi|$ are their conjugate transposed row vectors ψ^* and (85) is the standard inner product $\psi_1^* \psi_2$ (with conjugation of the first argument).

The *proof* of this very important result is somewhat technical and will be given in the appendix.

(Since we have identified E with an algebra of linear operators in a Hilbert space standard spectral analysis now permits getting spectral resolutions also for Hermitian quantities that are not quantized, but we do not discuss this further.)

It is useful to define the linear *rank 1 operator* $|\psi_1\rangle\langle\psi_2|$ on H , which maps any $|\psi\rangle$ to the multiple $|\psi_1\rangle\langle\psi_2|\psi\rangle = \langle\psi_2|\psi\rangle|\psi_1\rangle$ of $|\psi_1\rangle$. One easily calculates

$$(86) \quad \text{tr } |\psi_1\rangle\langle\psi_2| = \langle\psi_2|\psi_1\rangle.$$

By direct calculation we see that

$$E_n = |n\rangle\langle n|,$$

and (77) can be rewritten as

$$(87) \quad f(A^{(1)}, \dots, A^{(s)}) = \sum_n f(A_n^{(1)}, \dots, A_n^{(s)}) |n\rangle\langle n|;$$

in particular

$$(88) \quad A^{(k)} = \sum_n A_n^{(k)} |n\rangle\langle n|,$$

$$(89) \quad 1 = \sum_n |n\rangle\langle n|,$$

and therefore for all $A, B \in E$,

$$(90) \quad AB = \sum_n A|n\rangle\langle n|B.$$

But note that E need not contain all rank 1 operators; for example,

$$(91) \quad |m\rangle\langle n| \in E \text{ only when } m \equiv n,$$

where \equiv is the equivalence relation derived in the proof of Theorem 6.5. We therefore see that in general, E is only a subalgebra of the algebra of all linear operators on H . In particular, when E is commutative the E consists of diagonal operators only. In general, (91) justifies so-called *superselection rules* in quantum mechanics.

Finally we mention that the *pure states* of quantum theory, corresponding to wave functions $|\psi\rangle$ of norm 1 and defined by the expectation

$$(92) \quad \langle A \rangle := \langle \psi | A | \psi \rangle,$$

can be written in terms of the density

$$(93) \quad \rho := |\psi\rangle\langle\psi|$$

as

$$(94) \quad \langle A \rangle = \text{tr} (A\rho).$$

Unless $|\mathcal{N}| = 1$, $\log \rho$ does not exist (since ρ has zero eigenvalues); hence pure states are not ensembles. However, by (87), any ensemble with quantized entropy can be written as a so-called *mixture* of entropy eigenstates $|n\rangle$, since

$$(95) \quad \rho = \sum \rho_n |n\rangle\langle n|$$

where

$$(96) \quad \rho_n = e^{-S_n/k} > 0, \quad \sum \rho_n = 1,$$

and hence

$$(97) \quad \langle A \rangle = \text{tr} \left(\sum \rho_n |n\rangle\langle n| A \right) = \sum \rho_n \langle n | A | n \rangle.$$

Since classical quantum mechanics works without explicit volume (so $V = 1$) and fixed particle numbers, the entropy is a linear function of the internal energy, $S = \beta H + \text{const}$; hence the eigenstates of the entropy are precisely the eigenstates of the Hamiltonian H , and with $B = \beta H$, the partition function (19 of Theorem 3.3 takes the familiar form

$$Z = \sum_{n \in \mathcal{N}} e^{-\beta H_n}.$$

Thus we recover the full formal apparatus of (static) quantum mechanics by spectral analysis of the entropy (or the Hamiltonian).

We conclude that, in our setting, pure states appear simply as abstractions useful for the analysis of arbitrary ensembles in the same way that arbitrary wave pattern in ordinary space can be profitably analyzed as a mixture of plane waves. There is no need to assign to them any deeper significance, since they are no longer at the very roots of the tree of physics.

Aspect experiment: noncommutativity is essential

7. Logic, Probability and Measurement

We now investigate how to formulate in our framework statements about a particular physical system that can be meaningfully held to be true or false, so-called propositions (not to be confused with the mathematical Propositions in our development of the subject). The set of possible truth values (answers) consists of 0 (false) and 1 (true) only, and Proposition 6.2 suggests the following definition, cf. von Neumann [18]. However, we emphasize that all results of this section are completely independent of quantization.

7.1. Definition. A *proposition* is a Hermitean idempotent, i.e., a quantity $E \in \mathbb{E}$ such that

$$(98) \quad E^2 = E = E^* .$$

Two propositions E_1, E_2 are called *mutually exclusive* if $E_1 E_2 = 0$ (and hence also $E_2 E_1 = (E_1^* E_2^*)^* = (E_1 E_2)^* = 0$).

For example the idempotents E_n constructed in Proposition 6.3 have a natural interpretation as propositions

$$\text{“}A^{(1)}, \dots, A^{(s)} \text{ attained the values } A_n^{(1)}, \dots, A_n^{(s)}\text{”} .$$

These propositions are mutually exclusive.

PROPOSITION 7.1.

- (i) If E is a proposition then $E' = 1 - E$ is a proposition.
- (ii) If E_1, \dots, E_m are mutually exclusive propositions then $E = E_1 + \dots + E_m$ is a proposition.

PROOF.

- (i) Clearly E' is Hermitean, and $E'^2 = (1 - E)^2 = 1 - 2E + E^2 = 1 - E = E'$.
- (ii) Clearly E is Hermitean, and $E^2 = (\sum_i E_i)(\sum_k E_k) = \sum_{i,k} E_i E_k = \sum_i E_i = E$.

□

It is easy to see that the natural interpretation of $1 - E$ is as the proposition
“ E is false”

and that of $E_1 + \dots + E_m$ is
“One of E_1, \dots, E_m is true”.

In particular, since the Hermitean idempotents E_n constructed in Proposition 6.3 are mutually exclusive, we see that the assertion that a family of pairwise commuting quantized quantities takes in a measurement values from a given subset of the joint spectrum can be formulated as a proposition in the present sense and hence is meaningful; and using more general spectral resolutions this also holds without the quantization assumption. Since a single Hermitean quantity A is trivially “commuting”, it is also meaningful to ask whether A has taken values from a given subset of the spectrum of A .

For commuting propositions we can reconstruct classical logic (note that in particular mutually exclusive propositions commute):

THEOREM 7.2.

(i) *If E_1 and E_2 are commuting propositions then*

$$(99) \quad \neg E_1 := 1 - E_1 \quad (\text{“not } E_1\text{”})$$

$$(100) \quad E_1 \wedge E_2 := E_1 E_2 \quad (\text{“} E_1 \text{ and } E_2\text{”})$$

$$(101) \quad E_1 \vee E_2 := E_1 + E_2 - E_1 E_2 \quad (\text{“} E_1 \text{ or } E_2\text{”})$$

are again propositions.

(ii) *The propositions in a commutative subalgebra E_c of E form a Boolean algebra, i.e., the following laws hold:*

$$(B1) \quad \neg 0 = 1,$$

$$(B2) \quad E \wedge (\neg E) = 0,$$

$$(B3) \quad (\neg E_1) \wedge (\neg E_2) = \neg(E_1 \vee E_2),$$

$$(B4) \quad E_1 \wedge E_2 = E_2 \wedge E_1,$$

$$(B5) \quad (E_1 \wedge E_2) \wedge E_3 = E_1 \wedge (E_2 \wedge E_3),$$

$$(B6) \quad E_1 \wedge (E_1 \vee E_2) = E_1,$$

$$(B7) \quad E_1 \wedge (E_2 \vee E_3) = (E_1 \wedge E_2) \vee (E_1 \wedge E_3).$$

(These imply all other laws of classical logic).

PROOF.

(i) $\neg E_1$ is a proposition by Proposition 7.1. $E_1 E_2$ is Hermitean since $(E_1 E_2)^* = E_2^* E_1^* = E_2 E_1 = E_1 E_2$ and idempotent since $(E_1 E_2)^2 = E_1 E_2 E_1 E_2 = E_1^2 E_2^2 = E_1 E_2$. Finally, $E_1 + E_2 - E_1 E_2 = 1 - (1 - E_1)(1 - E_2) = \neg((\neg E_1) \wedge (\neg E_2))$ is a proposition.

(ii) is straightforward.

□

If two propositions E_1 and E_2 do not commute then E_1E_2 is not even Hermitean, and if we try to remedy this by using $\frac{1}{2}(E_1E_2 + E_2E_1)$ instead, this is not idempotent. Thus the above theorem, and hence classical logic, depends on commutativity in an essential way. It is possible to generalize classical logic in a different way that also applies for noncommuting propositions (von Neumann [18]), by using the concept of *implication* as the basic relation of propositions. However, the resulting *quantum logic* is rather clumsy and has not lead to useful applications, so we do not discuss it in detail.

PROPOSITION 7.3. *The relation \Rightarrow defined on the set of all propositions by*

$$E_1 \Rightarrow E_2 \text{ ("}E_1 \text{ implies } E_2\text{")} \text{ iff } E_2 - E_1 \text{ is a proposition ("}E_2 \text{ but not } E_1\text{")}$$

is reflexive and transitive.

PROOF. Straightforward. □

We now assume that some state $\langle \cdot \rangle$ is given that specifies the experimental conditions in which a proposition is formulated.

PROPOSITION 7.4. *Let E be a proposition with $\langle E \rangle = p$. Then $0 \leq p \leq 1$ and*

$$(102) \quad \sigma(E) := \sqrt{\langle (E - p)^2 \rangle} = \sqrt{p(1 - p)}.$$

PROOF. Since E is Hermitean, p is real. Hence

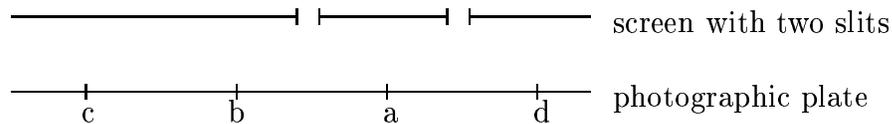
$$\begin{aligned} 0 \leq \langle (E - p)^*(E - p) \rangle &= \langle (E - p)^2 \rangle = \\ \langle E^2 - 2pE + p^2 \rangle &= \langle (1 - 2p)E + p^2 \rangle = \\ &= (1 - 2p)\langle E \rangle + p^2 = (1 - 2p)p + p^2 = p(1 - p). \end{aligned}$$

This shows that $p(1 - p) \geq 0$, hence $0 \leq p \leq 1$, and at the same time proves (102). □

We interpret $p = \langle E \rangle$ as the *probability* that the proposition E is true. Thus probability is an expression of the expectation of how likely the proposition is to be true; in particular, it can be calculated even for unique situations. The standard deviation (102) expresses the likely deviation from the expectation. For p close to 0 or 1, the standard deviation is small and shows that we may be rather confident that the proposition is false or true, respectively, though not as confident

as one might think: For $p = 10^{-4}$, the standard deviation is only $\sigma \approx 10^{-2}$! For $p = \frac{1}{2}$, the standard deviation is $\sigma = \frac{1}{2}$ which expresses the fact that for a *single* experiment any outcome is reasonable.

As an illustration, we discuss a double slit experiment where photons pass through a screen with two close and narrow slits:



We consider the proposition $E_l(x)$ that a photon recorded on the photographic plate at position x went through the left slit. Then $E_r(x) = \neg E_l(x) = 1 - E_l(x)$ is the proposition that the photon went through the right slit. We consider first the symmetric position $x = a$. By symmetry, $\langle E_l(a) \rangle = \langle E_r(a) \rangle = \langle 1 - E_l(a) \rangle = 1 - \langle E_l(a) \rangle$ whence $\langle E_l(a) \rangle = \langle E_r(a) \rangle = \frac{1}{2}$, and we conclude that it is equally likely that the photon went through either slit. In position $x = b$ we would think that $\langle E_l(b) \rangle > \langle E_r(b) \rangle = 1 - \langle E_l(b) \rangle$ (details depend, of course, on quantum mechanical calculations), giving $\langle E_l(b) \rangle > \frac{1}{2} > \langle E_r(b) \rangle$, and we conclude that it is likely that the photon went through the left slit and more unlikely (though possible) that it went through the right slit. This holds even more so in position c while in position d it is most likely that the photon went through the right slit. Thus a maximum likelihood argument would predict that (most) photons arriving to the left (right) of position a went through the left (right) slit.

Traditional discussions of the double slit experiment wonder whether a photon can go through both slits simultaneously. Since $E_l(x)$ and $E_r(x) = 1 - E_l(x)$ commute, this question is meaningful and given by the proposition $E_{\text{both}} = E_l(x)E_r(x)$, whence $\langle E_{\text{both}} \rangle = \langle E_l(x)E_r(x) \rangle = \langle E_l(x)(1 - E_l(x)) \rangle = \langle E_l(x) - E_l(x)^2 \rangle = \langle 0 \rangle = 0$. Thus there is zero probability that any photon goes through both slits. A similar calculation shows that with probability one, each photon goes through one of the slits. Thus each photon passes a unique slit. This analysis is independent of whether the experiment is performed with small balls (i.e., classical particles) or with photons (i.e., quantum particles); only the detailed interaction and hence the numerical values of the expectations change.

We conclude that it is consistent with our interpretation of quantum theory to assign a photon a unique path (though it cannot be well predicted or well measured in most microscopic situations). This will be made more explicit in a subsequent paper where we discuss dynamics. The reason for the strange microscopic be-

haviour of quantum particles is the inseparability due to failure of classical logic and the resulting nonlocality; *not* the lack of a path “between observations”: One must visualize a quantum particle as having a kind of *quantum eyes* (mathematically described by the wave function!) which give it some information about its neighbourhood (exponentially decaying with distance, causing the inseparability) to which it responds in its own dynamics.

The interpretation of probability has been surrounded by philosophical puzzles for a long time; Fine [5] is probably still the best discussion of the problems involved. Our next result gives clear support to the conclusion of M. Drieschner: “Wahrscheinlichkeit ist vorausgesagte relative Häufigkeit” (probability is predicted relative frequency; [4], p.73). More precisely, we may formulate: For repeated experiments, the probability carries the information of *expected relative frequency*.

PROPOSITION 7.5. *Let E_1, \dots, E_m be propositions with probability p . Then:*

(i) *The expectation of the relative frequency*

$$(103) \quad Q := \frac{1}{m}(E_1 + \dots + E_m)$$

is p .

(ii) (Law of large numbers) *If E_1, \dots, E_m are uncorrelated in the sense that*

$$(104) \quad \langle E_i E_k \rangle = \langle E_i \rangle \langle E_k \rangle \text{ for } i \neq k,$$

then the standard deviation of the relative frequency is

$$\sigma(Q) = \sqrt{\frac{p(1-p)}{m}}$$

and becomes arbitrarily small as m becomes large.

(iii) *If E_1, \dots, E_m are mutually exclusive then $p \leq \frac{1}{m}$ and $\sigma(Q) = \sqrt{p(\frac{1}{m} - p)}$.*

PROOF. (i) follows from

$$\langle Q \rangle = \frac{1}{m}(\langle E_1 \rangle + \dots + \langle E_m \rangle) = \frac{1}{m}(p + \dots + p) = p.$$

For (ii) and (iii) we note first that

$$(105) \quad Q^2 = \frac{1}{m^2} \left(\sum_i E_i \right) \left(\sum_k E_k \right) = \frac{1}{m^2} \sum_{i,k} E_i E_k.$$

In case (ii), (104) implies that in the expectation of this sum we get $m^2 - m$ contributions of size $\langle E_i \rangle \langle E_k \rangle = p^2$ and m contributions of size $\langle E_i^2 \rangle = \langle E_i \rangle = p$. Hence $\langle Q^2 \rangle = (mp + (m^2 - m)p^2)/m^2$ and

$$\sigma(Q)^2 = \langle (Q - p)^2 \rangle = \langle Q^2 \rangle - 2p\langle Q \rangle + p^2$$

simplifies to $p(1 - p)/m$.

And in case (iii), we get instead $m^2 - m$ contributions of size zero, resulting in $\langle Q^2 \rangle = mp/m^2$ and $\sigma(Q)^2 = p(\frac{1}{m} - p)$. \square

It is now easy to recover the standard probability interpretation of quantum mechanics. To this end we consider the orthonormal basis of eigenvectors constructed in Theorem 6.5, and interpret the Hermitean idempotent

$$E_n = |n\rangle\langle n|$$

as the proposition that a system can be considered to be in the entropy (or energy) eigenstate $|n\rangle$. Actually, the system will be in a state $\langle \cdot \rangle$ with density ρ , and the probability that it can be considered as being in the pure state defined by $|n\rangle$ is

$$(106) \quad \rho_n := \langle E_n \rangle = \text{tr} (E_n \rho) = \text{tr} |n\rangle\langle n| \rho = \langle n | \rho | n \rangle.$$

Since an arbitrary function A of $A^{(1)}, \dots, A^{(s)}$ is representable, by Theorem 6.3, as

$$(107) \quad A = \sum A_n |n\rangle\langle n|,$$

we have $A|n\rangle = A_n|n\rangle$. Thus the A_n are the eigenvalues of A , and

$$(108) \quad \langle A \rangle = \text{tr} (A\rho) = \sum A_n \text{tr} |n\rangle\langle n| \rho = \sum A_n \rho_n$$

is indeed an average of the values that A takes in the states $|n\rangle$, weighted according to their probability.

However, we emphasize again that pure states should not be regarded as the results of “ideal measurements” but rather as highly idealized partial states occurring in the spectral analysis of realistic ensembles. In this way, all speculations about the “collapse of the wave function” in an ideal measurement become superfluous, though collapse can be proved in some idealized situations from dynamical assumptions via contact with the surrounding; see e.g. Gisin & Percival [7].

discuss more measurement results Braginsky & Khalili [1].
derive Kolmogorov axioms in the commutative case
remarks on chance, uncertainty, triple slit

8. Fluctuations and response functions

Response functions are the thermodynamic functions most accessible to experiment. They predict how some thermodynamic variable responds to changes of an intensive variable while certain other thermodynamic variables remain fixed. Response functions are expressible as a 1-form divided by the differential of some intensive variable, and this suffices to calculate them from an equation of state using the first law and the Gibbs–Duhem equation. Typical examples are the *heat capacities*

$$(109) \quad C_V = \left(\frac{T d\bar{S}}{dT} \right)_{\bar{V}} \quad \text{and} \quad C_P = \left(\frac{T d\bar{S}}{dT} \right)_P,$$

which describe the amount of heat $dQ = T dS$ needed to raise the temperature by one (strictly speaking, infinitesimal) unit, under conditions of fixed volume \bar{V} or pressure P (indicated by an index). Other response functions of interest are the *isothermal* and *adiabatic compressibility*,

$$(110) \quad K_T = \left(\frac{-\bar{V}^{-1} d\bar{V}}{dP} \right)_T \quad \text{and} \quad K_S = \left(\frac{-\bar{V}^{-1} d\bar{V}}{dP} \right)_S,$$

and the *thermal expansivity*

$$(111) \quad \alpha_P = \left(\frac{\bar{V}^{-1} d\bar{V}}{dT} \right)_P,$$

which measure the relative change of volume under a unit pressure change and unit temperature change, respectively.

When the set of extensive variables commutes (as in all macroscopic equilibrium situations), such response functions can be related to *covariances* of extensive variables, thus indicating a connection to microscopic fluctuations (which is made more precise by fluctuation–dissipation theorems of nonequilibrium thermodynamics).

In order to show this, we need first a way to compute covariances.

PROPOSITION 8.1. *If the extensive variables H and $a_j (j \in J)$ are pairwise commuting then*

$$(112) \quad \left\langle (A - \bar{A})(S - \bar{S}) \right\rangle = \kappa T \left(\frac{\partial \bar{A}}{\partial T} - \left\langle \frac{\partial A}{\partial T} \right\rangle \right),$$

$$(113) \quad \left\langle (A - \bar{A})(a_j - \bar{a}_j) \right\rangle = \kappa T \left(\frac{\partial \bar{A}}{\partial g_j} - \left\langle \frac{\partial A}{\partial g_j} \right\rangle \right),$$

for all continuously differentiable functions A of T , g , H and a .

■ check notes. apparently we need V to be a real number. Why?

PROOF. The assumption implies that A commutes with the entropy

$$S = T^{-1}(H - g \cdot a).$$

Hence we can apply Proposition 9.1 of the appendix to compute

$$\begin{aligned} d\bar{A} &= d \operatorname{tr} \left(A e^{-S/\kappa} \right) = \operatorname{tr} \left(e^{-S/\kappa} dA \right) + \operatorname{tr} \left(A e^{-S/\kappa} \left(-\frac{1}{\kappa} \right) dS \right) \\ &= \operatorname{tr} \left(e^{-S/\kappa} dA \right) + \operatorname{tr} \left(e^{-S/\kappa} AdS \right) / \kappa, \end{aligned}$$

giving

$$(114) \quad d\bar{A} = \langle dA \rangle + \langle AdS \rangle / \kappa.$$

Now

$$\begin{aligned}
& \left\langle (A - \bar{A})(S - \bar{S}) \right\rangle dT + \left\langle (A - \bar{A})(a - \bar{a}) \right\rangle \cdot dg \\
&= \left\langle (A - \bar{A}) \left((S - \bar{S}) dT + (a - \bar{a}) \cdot dg \right) \right\rangle \\
&= \left\langle (A - \bar{A}) \left((SdT + a \cdot dg) - (\bar{S}dT + \bar{a} \cdot dg) \right) \right\rangle \\
&= \left\langle (A - \bar{A}) (-TdS - 0) \right\rangle \quad \text{by (46) and (45)} \\
&= T \langle AdS \rangle - T\bar{A} \langle dS \rangle \\
&= T \langle AdS \rangle \quad \text{by (47)} \\
&= \kappa T \left(d\bar{A} - \langle dA \rangle \right) \quad \text{by (114)}.
\end{aligned}$$

Thus, for arbitrary reversible transformations, we find

$$\left\langle (A - \bar{A})(S - \bar{S}) \right\rangle \frac{dT}{d\lambda} + \left\langle (A - \bar{A})(a - \bar{a}) \right\rangle \cdot \frac{dg}{d\lambda} = \kappa T \left(\frac{d\bar{A}}{d\lambda} - \left\langle \frac{dA}{d\lambda} \right\rangle \right).$$

By choosing $\lambda = T$ and $\lambda = g_j$, respectively, (112) and (113) follow. \square

As special cases we obtain formulae for the fluctuations of extensive variables.

THEOREM 8.2. *If the extensive variables H and $a_j (j \in J)$ are pairwise commuting then*

$$(115) \quad \left\langle (S - \bar{S})^2 \right\rangle = \kappa T \frac{d\bar{S}}{dT},$$

$$(116) \quad \left\langle (a_i - \bar{a}_i)(S - \bar{S}) \right\rangle = \kappa T \frac{d\bar{a}_i}{dT} \quad (i \in J),$$

$$(117) \quad \left\langle (a_i - \bar{a}_i)(a_j - \bar{a}_j) \right\rangle = \kappa T \frac{d\bar{a}_i}{dg_j} \quad (i, j \in J),$$

and we have the reciprocity relations

$$(118) \quad \frac{d\bar{a}_i}{dg_j} = \frac{d\bar{a}_j}{dg_i}, \quad \frac{d\bar{a}_i}{dT} = \frac{d\bar{S}}{dg_i}.$$

PROOF. Insert $A = S$ and $A = a_i$ into (112) and (113) to get (115), (116),

$$(119) \quad \left\langle (S - \bar{S})(a_j - \bar{a}_j) \right\rangle = \bar{k}T \frac{dS}{dg_j},$$

and (117). By commutativity, (117) and a comparison of (116) with (119) give the reciprocity relations. \square

8.x. Remarks. (i) Note that since \bar{k} is very small, fluctuations are $O(\bar{k})$ and hence negligible unless the system considered is very tiny. An exception is at critical points where the expectation of extensive variables is not differentiable and their derivatives can become huge.

(ii) Higher order central moments can be obtained in the same way, substituting more complicated expressions for A and using the formulas for the lower order moments to evaluate the right hand side of (112) and (113). It is easy to check that higher order moments are also of higher order in \bar{k} .

COROLLARY 8.3. *The matrix*

$$(120) \quad \Sigma := \begin{pmatrix} \frac{d\bar{S}}{dT} & \frac{d\bar{S}}{dg} \\ \frac{d\bar{S}}{d\bar{a}} & \frac{d\bar{S}}{d\bar{a}} \\ \frac{d\bar{S}}{dT} & \frac{d\bar{S}}{dg} \end{pmatrix}$$

is symmetric and positive semidefinite; in particular,

$$(121) \quad \frac{d\bar{S}}{dT} \geq 0, \quad \frac{d\bar{a}_j}{dg_j} \geq 0 \quad (j \in J).$$

PROOF. Symmetry follows from (118), and semidefiniteness from

$$\begin{aligned}
\begin{pmatrix} \omega \\ u \end{pmatrix}^T \Sigma \begin{pmatrix} \omega \\ u \end{pmatrix} &= \omega^2 \frac{d\bar{S}}{dT} + \omega \left(\frac{d\bar{S}}{dg} u + u^T \frac{d\bar{a}}{dT} \right) + u^T \frac{d\bar{a}}{dg} u \\
&= \frac{1}{\hbar T} \left(\omega^2 \langle (S - \bar{S})^2 \rangle + \omega \langle (S - \bar{S})(a - \bar{a}) \rangle \right. \\
&\quad \left. + \omega \langle u \cdot (a - \bar{a})(S - \bar{S}) \rangle + \langle u \cdot (a - \bar{a})(a - \bar{a}) \cdot u \rangle \right) \\
&= \frac{1}{\hbar T} \left\langle \left(\omega(S - \bar{S}) + (a - \bar{a}) \cdot u \right)^2 \right\rangle \geq 0
\end{aligned}$$

since S and a are Hermitean. Since a positive semidefinite matrix has nonnegative diagonal entries, (121) follows; but (121) can also be seen directly since these response functions are proportional to the expectation of $(S - \bar{S})^2$ and $(a_j - \bar{a}_j)^2$, respectively. \square

Note that, in contrast to our approach, (121) is usually derived from the assumed second law as a *stability condition*.

COROLLARY 8.4. *For a chemical system,*

$$\begin{aligned}
\langle (S - \bar{S})^2 \rangle &= \hbar C_p, \\
\langle (N - \bar{V})^2 \rangle &= \hbar T \bar{V} K_T;
\end{aligned}$$

in particular $C_p \geq 0$, $K_T \geq 0$.

PROOF. Use (115), (117) and (109), (111). \square

renormalization?

9. Appendix: Auxiliary Results and Proofs

In this section we prove some technical results needed for proofs in Sections 4–8, and give the proof of Theorem 6.5.

PROPOSITION 9.1. *Let A, B be quantities depending continuously differentiable on a parameter λ , and suppose that*

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

Thus for any continuously differentiable function f of two variables,

$$(122) \quad \frac{d}{d\lambda} \operatorname{tr} f(A, B) = \operatorname{tr} \partial_1 f(A, B) \frac{dA}{d\lambda} + \operatorname{tr} \partial_2 f(A, B) \frac{dB}{d\lambda} .$$

PROOF. We proof the special case $f(x, y) = x^m y^n$, where (122) reduces to

$$(123) \quad \frac{d}{d\lambda} \operatorname{tr} A^m B^n = \operatorname{tr} (mA^{m-1} B^n \frac{dA}{d\lambda}) + \operatorname{tr} (nA^m B^{n-1} \frac{dB}{d\lambda}) .$$

The general case then follows for polynomials $f(x, y)$ by taking suitable linear combinations, and for arbitrary f by taking suitable limits. To prove (123), we note that

$$\begin{aligned} \frac{d}{d\lambda} \operatorname{tr} (A_1 \dots A_{m+n}) &= \operatorname{tr} \frac{d}{d\lambda} (A_1 \dots A_{m+n}) \\ &= \operatorname{tr} \sum_{j=1}^{m+n} A_1 \dots A_{j-1} \frac{dA_j}{d\lambda} A_{j+1} \dots A_{m+n} \\ &= \sum_{j=1}^{m+n} \operatorname{tr} A_1 \dots A_{j-1} \frac{dA_j}{d\lambda} A_{j+1} \dots A_{m+n} \\ &= \sum_{j=1}^{m+n} \operatorname{tr} A_{j+1} \dots A_{m+n} A_1 \dots A_{j-1} \frac{dA_j}{d\lambda} , \end{aligned}$$

using the cyclic commutativity of the trace. If we specialize to $A_j = A$ if $j \leq m$, $A_j = B$ if $j > m$, and note that A and B commute, we arrive at (123). \square

(Note that we assumed that we can interchange trace and differentiation, and approximate f — on the joint spectrum of (A, B) — by polynomials. In a completely rigorous treatment, this would have to be justified; but being slightly sloppy here allows to keep the mathematical machinery at a lower level.)

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

COROLLARY 9.2. *For any quantity A depending continuously differentiable on a parameter λ , and any continuously differentiable function f of a single variable,*

$$(124) \quad \frac{d}{d\lambda} \operatorname{tr} f(A) = \operatorname{tr} f'(A) \frac{dA}{d\lambda}.$$

PROPOSITION 9.3. (*Klein inequality*). *Suppose that*

$$(125) \quad \sum_l f_l(\alpha) g_l(\beta) \geq 0 \text{ for all } \alpha, \beta \in \mathbb{R},$$

Then, for all Hermitean quantities A and B for which the left hand side is defined,

$$(126) \quad \operatorname{tr} \sum_l f_l(A) g_l(B) \geq 0.$$

Moreover, if equality in (125) implies $\alpha = \beta$ then equality in (126) implies $A = B$, and if equality in (125) implies $\alpha = 0$ then equality in (126) implies $A = 0$.

PROOF. This is trivial for the expectation algebra used in Section 1. We prove here the result for $\mathbb{E} = \mathbb{C}^{m \times m}$; the same argument works also in more general situations (cf. e.g. Thirring [22], §2.2) if we use spectral resolutions and integrals.

So let A and B be Hermitean $m \times m$ -matrices. Then there exist a complete orthonormal system of eigenpairs $(\alpha_1, \phi_1), \dots, (\alpha_m, \phi_m)$ of A and another complete orthonormal system of eigenpairs $(\beta_1, \psi_1), \dots, (\beta_n, \psi_n)$ of B . Expressed in these eigensystems we have

$$f_l(A) = \sum_i f_l(\alpha_i) \phi_i \phi_i^*, \quad g_l(B) = \sum_k g_l(\beta_k) \psi_k \psi_k^*,$$

hence

$$\begin{aligned}
\text{tr} \sum_l f_l(A) g_l(B) &= \text{tr} \left(\sum_{i,k,l} f_l(\alpha_i) g_l(\beta_k) \phi_i \phi_i^* \psi_k \psi_k^* \right) \\
&= \left(\sum_{i,k,l} f_l(\alpha_i) g_l(\beta_k) \text{tr} \phi_i \phi_i^* \psi_k \psi_k^* \right) \\
(127) \qquad &= \sum_{i,k} \left(\sum_l f_l(\alpha_i) g_l(\beta_k) \right) |\phi_i^* \psi_k|^2 \geq 0
\end{aligned}$$

since

$$\text{tr} \phi_i \phi_i^* \psi_k \psi_k^* = \phi_i^* \psi_k \text{tr} \phi_i \psi_k^* = \phi_i^* \psi_k \cdot \psi_k^* \phi_i = \phi_i^* \psi_k \cdot (\phi_i^* \psi_k)^* = |\phi_i^* \psi_k|^2$$

If equality in (125) implies $\alpha = \beta$ and equality holds in (126) then equality holds in (127). Therefore

$$\phi_i^* \psi_k = 0 \text{ whenever } \alpha_i \neq \beta_k$$

Thus if $\alpha_i \neq \lambda$ then ϕ_i^* is orthogonal to all eigenvectors of B corresponding to eigenvalues $\beta_k \neq \lambda$, and hence must itself be an eigenvector of B corresponding to the eigenvalue λ . Since this holds for all i , we see that A and B have precisely the same eigenvalues and corresponding eigenspaces, and we can choose the eigenvectors such that $\alpha_i = \beta_i$, $\phi_i = \psi_i$ for all i . Hence $A = \sum \alpha_i \phi_i \phi_i^* = \sum \beta_i \psi_i \psi_i^* = B$.

If equality in (125) implies $\alpha = 0$ then equality in (126) implies similarly that

$$\phi_i^* \psi_k = 0 \text{ whenever } \alpha_i \neq 0.$$

Since this holds for all k , $\phi_i = 0$ for $\alpha_i \neq 0$, contradiction. Hence all α_i vanish, and $A = \sum \alpha_i \phi_i \phi_i^* = 0$. \square

COROLLARY 9.4. *Suppose that $f(\alpha) \geq 0$ for all $\alpha \in \mathbb{R}$, with equality only for $\alpha = 0$. Then $\langle f(A) \rangle \geq 0$ for all Hermitean A and every ensemble $\langle \cdot \rangle$, with equality only for $A = 0$.*

PROOF. $\langle f(A) \rangle = \text{tr} f(A) e^{-S/k} \geq 0$ by Klein's inequality applied with $g(\beta) = e^{-\beta/k}$, and equality implies $A = 0$. \square

PROPOSITION 9.5. (*Cauchy–Schwarz inequality*). For any state,

$$(128) \quad |\langle AB^* \rangle|^2 \leq \langle AA^* \rangle \langle BB^* \rangle .$$

PROOF. For arbitrary $\alpha, \beta \in \mathbb{C}$ we have

$$\begin{aligned} 0 &\leq \langle (\alpha A - \beta B)(\alpha A - \beta B)^* \rangle \\ &= \alpha\alpha^* \langle AA^* \rangle - \alpha\beta^* \langle AB^* \rangle - \beta\alpha^* \langle BA^* \rangle + \beta\beta^* \langle BB^* \rangle \\ &= |\alpha|^2 \langle AA^* \rangle - 2\operatorname{Re}(\alpha\beta^* \langle AB^* \rangle) + |\beta|^2 \langle BB^* \rangle \end{aligned}$$

We now choose $\beta = \langle AB^* \rangle$, and obtain for arbitrary real α the inequality

$$(129) \quad 0 \leq \alpha^2 \langle AA^* \rangle - 2\alpha |\langle AB^* \rangle|^2 + |\langle AB^* \rangle|^2 \langle BB^* \rangle .$$

Now $\langle BB^* \rangle \geq 0$ by (E4). If $\langle BB^* \rangle = 0$ then this forces $\langle AB^* \rangle = 0$ since otherwise a tiny α produces a negative right hand side in (129). And if $\langle BB^* \rangle > 0$ we can choose $\alpha = \langle BB^* \rangle$ and obtain

$$0 \leq \langle BB^* \rangle^2 \langle AA^* \rangle - \langle BB^* \rangle |\langle AB^* \rangle|^2 .$$

After division by $\langle BB^* \rangle$, we find again (128). \square

Finally, we present the proof of Theorem 6.5.

PROOF. We want to show that \mathbb{E} is a direct sum of full operator algebras, i.e., can be viewed (in the basis $|n\rangle$, $n \in \mathcal{N}$) as the algebra of block-diagonal matrices indexed by \mathcal{N} , with blocks defined by the partition of \mathcal{N} induced by an equivalence relation \equiv .

Our first aim is to identify, in steps (i)–(iii), vector spaces V_{mn} corresponding to the set of matrices which are zero everywhere except in position (m, n) . Then, in step (iv), we construct the equivalence relation \equiv , and in the final steps (v)–(vi), we produce the Hilbert space.

(i) We first note that (77) implies

$$(130) \quad 1 = \sum_n E_n,$$

whence any quantity A can be written as

$$(131) \quad A = \left(\sum_m E_m \right) A \left(\sum_n E_n \right) = \sum_{m,n} E_m A E_n.$$

We analyze the various terms in the sum (131).

(ii) For $m = n$,

$$\begin{aligned} (E_n A E_n) A^{(k)} &\stackrel{(77)}{=} E_n A E_n \left(\sum_l A_l^{(k)} E_l \right) = \sum_l A_l^{(k)} E_n A E_n E_l \\ &\stackrel{(75),(76)}{=} A_n^{(k)} E_n A E_n = \sum_l A_l^{(k)} E_l E_n A E_n \\ &= \left(\sum_l A_l^{(k)} E_l \right) E_n A E_n = A^{(k)} (E_n A E_n). \end{aligned}$$

Since the $A^{(k)}$ form a maximal system of commuting quantities, $E_n A E_n$ is a function of the $A^{(k)}$. It follows from (77) that $E_n A E_n$ is a linear combination of the E_l ; multiplication with E_n and use of the orthogonality relations (75), (76) then implies that $E_n A E_n$ is a multiple of E_n ,

$$(132) \quad E_n A E_n = A_{nn} E_n \quad \text{for some } A_{nn} \in \mathbb{C}.$$

(iii) For fixed $m, n \in \mathcal{N}$ we consider the vector spaces V_{mn} of all products

$$(133) \quad \hat{A} := E_m A E_n \quad (A \in \mathbb{E}).$$

Note that by (132), $\hat{A}^* \hat{B} = E_n A^* E_m B E_n$ is a multiple of E_n , and since

$$(134) \quad \text{tr } E_n = 1$$

by Corollary 6.4 and nondegeneracy, we find

$$(135) \quad \hat{A}^* \hat{B} = \text{tr} (\hat{A}^* \hat{B}) E_n.$$

Similarly, $\hat{B} \hat{A}^*$ is a multiple of E_m and we find

$$(136) \quad \hat{B} \hat{A}^* = \text{tr} (\hat{B} \hat{A}^*) E_m = \text{tr} (\hat{A}^* \hat{B}) E_m.$$

Note that (135) implies that $\text{tr} (\hat{A}^* \hat{B})$ is finite; and by the trace axioms, this expression defines an inner product on V_{mn} .

Now suppose that $\dim V_{mn} > 1$. Then we can choose orthonormal quantities \hat{A}, \hat{B} , and from (135) and (136) we find

$$\hat{A}^* \hat{B} = 0, \quad \hat{A} \hat{A}^* = E_m, \quad \hat{B} \hat{B}^* = E_m.$$

Hence

$$0 = \hat{A}(\hat{A}^* \hat{B}) \hat{B}^* = (\hat{A} \hat{A}^*)(\hat{B} \hat{B}^*) = E_m E_m = E_m.$$

This contradicts $\text{tr } E_m = 1$, and we conclude that

$$(137) \quad \dim V_{mn} \leq 1 \quad \text{for all } m, n \in \mathcal{N}.$$

(iv) We now show that the relation \equiv defined by

$$(138) \quad m \equiv n : \iff \dim V_{mn} = 1$$

is an equivalence relation. Reflexivity follows directly from (ii), and symmetry holds since $\hat{A} \in V_{mn} \Rightarrow \hat{A}^* = E_n \hat{A} E_m \in V_{nm}$, and $\hat{A}^* \neq 0$ if $\hat{A} \neq 0$. To prove transitivity we note that $\hat{A} \in V_{lm}, \hat{B} \in V_{mn}$ implies $\hat{A} \hat{B} = E_l \hat{A} E_m \hat{B} E_n \in V_{ln}$. If $\hat{A} \hat{B} = 0$ then

$$\begin{aligned} 0 &= \hat{A}^*(\hat{A} \hat{B}) \hat{B}^* = (\hat{A}^* \hat{A})(\hat{B} \hat{B}^*) = \\ &= (\text{tr } \hat{A} \hat{A}^*) E_n (\text{tr } \hat{B} \hat{B}^*) E_n = (\text{tr } \hat{A} \hat{A}^*) (\text{tr } \hat{B} \hat{B}^*) E_n, \end{aligned}$$

which is impossible when $\hat{A}, \hat{B} \neq 0$.

(v) We now construct a special basis of E . Since \mathcal{N} is countable, every equivalence class of \equiv is countable, and its elements can be arranged as a finite or infinite sequence n_1, n_2, \dots . We pick quantities $\hat{T}_i \in V_{n_i, n_{i+1}}$, with $\text{tr } \hat{T}_i^* \hat{T}_i = 1$ and define

$$E_{n_i n_j} := \begin{cases} \hat{T}_i \hat{T}_{i+1} \dots \hat{T}_{j-1} & \text{if } i < j, \\ E_{n_i} & \text{if } i = j, \\ \hat{T}_j^* \hat{T}_{j+1}^* \dots \hat{T}_i^* & \text{if } i > j. \end{cases}$$

(To understand this construction we look at the matrix interpretation we aim at. E_{mn} is designed to be a matrix with a one in the (m, n) position and zeros elsewhere. The above complicated definition comes from the fact that we must account for the freedom to scale basis vectors of the Hilbert space by factors of absolute value 1. This freedom is picked up by choosing

the $\hat{T}_i = E_{n_i n_{i+1}}$, and the other E_{mn} are then determined by multiplication and transposition.)

Proceeding in this way for each equivalence class we find a family of quantities E_{mn} ($m, n \in \mathcal{N}$, $m \equiv n$) for which it is easily checked that $E_{mn} \in V_{mn}$ and

$$(139) \quad \text{tr } E_{nn} = 1, \quad \text{tr } E_{mn} = 0 \quad \text{if } m \neq n,$$

$$(140) \quad E_{nn} = E_n, \quad E_{mn}^* = E_{nm},$$

$$(141) \quad E_{lm} E_{mn} = E_{ln}, \quad E_{lm} E_{m'n} = 0 \quad \text{if } m \neq m'.$$

By (137) and (138), we have

$$E_m A E_n = \begin{cases} A_{mn} E_{mn} & \text{if } m \equiv n, \\ 0 & \text{otherwise} \end{cases}$$

for some number $A_{mn} \in \mathbb{C}$; therefore (131) implies that we can write any quantity $A \in \mathbb{E}$ uniquely as linear combination

$$(142) \quad A = \sum_{\substack{m, n \in \mathcal{N} \\ m \equiv n}} A_{mn} E_{mn}.$$

- (vi) Finally, we define a representation of \mathbb{E} on the Hilbert space H of all vectors indexed by \mathcal{N} , with standard inner product, by defining for $A \in \mathbb{E}$ given by (142) the image Ax of $x \in H$ by

$$(143) \quad (Ax)_m := \sum_{n \equiv m} A_{mn} x_n.$$

It is straightforward to check that this is a faithful representation of \mathbb{E} , i.e.

$$(A + B)x = Ax + Bx, \quad (\alpha A)x = \alpha(Ax),$$

$$(AB)x = A(Bx), \quad 1x = x,$$

$$Ax = 0 \text{ for all } x \in H \Rightarrow A = 0.$$

Moreover, the vectors $|n\rangle$ with entry 1 for index n and zero entries otherwise form an orthonormal basis of H . Since (143) implies

$$(144) \quad A|n\rangle = \sum_{m \equiv n} A_{mn} |m\rangle,$$

a comparison of (78) with (142) shows (82). Multiplying (144) by $\langle m|$ gives

$$(145) \quad A_{mn} = \langle m|A|n\rangle,$$

and by (142) and (139), we find

$$\operatorname{tr} A = \sum A_{mn} \operatorname{tr} E_{mn} = \sum A_{nn},$$

which implies (83). Finally,

$$A^* = \sum A_{mn}^* E_{mn}^* = \sum A_{mn}^* E_{nm}$$

by (142) and (140), whence

$$\langle m|A^*|n\rangle = A_{mn}^* = \langle n|A|m\rangle^*.$$

By taking linear combinations we find (84).

□

Relate to C*-Algebras (comments by Günther Hörmann)

Bibliography

- [1] V.B. Braginsky and F. Ya. Khalili, Quantum Measurement. Cambridge Univ. Press, Cambridge 1992.
- [2] L. Brillouin, Science and Information Theory. 2nd ed., Acad. Press, 1962.
- [3] P.A.M. Dirac, Lectures on Quantum Field Theory. Belfer Grad. School of Sci., New York 1966.
- [4] M. Drieschner, Voraussage – Wahrscheinlichkeit – Objekt. Über die begrifflichen Grundlagen der Quantenmechanik. Lecture Notes in Physics, Springer, Berlin, 1979.
- [5] T.L. Fine, Theory of Probability; an Examination of Foundations. Acad. Press, New York 1973.
- [6] J.W. Gibbs, Elementary Principles in Statistical Mechanics. Yale Univ. Press, New Haven 1902; reprinted, Dover 1960.
- [7] N. Gisin and I.C. Percival, The quantum-state diffusion model applied to open systems, J. Phys. A: Math. Gen. 25 (1992), 5677-5691.
- [8] D. Hilbert, Mathematische Probleme, Bull. Amer. Math. Soc. 8 (1902), 437-479.
- [9] H. Haken, Synergetic: An introduction. Springer, Berlin 1978.
- [10] K. Huang, Statistical Mechanics. 2nd ed., Wiley, New York 1987.
- [11] M. Jammer, Philosophy of Quantum Mechanics. Wiley, New York 1974.
- [12] E.T. Jaynes, Probability Theory in Science and Engineering. Socony Mobil Oil Co., Dallas 1958.
- [13] D.H. Krantz, R.D. Luce, P. Suppes, and A. Tversky, Foundations of Measurements, Vol. 1. Acad. Press, New York 1971.
- [14] L.D. Landau and E.M. Lifshits, Statistical Physics. 2nd engl. ed., Addison-Wesley, 1969.
- [15] R. D. Lee et al., Foundations of Measurements, Vol. 3. Acad. Press, San Diego 1990.
- [16] G. Ludwig, An axiomatic basis for quantum mechanics. 2 Vols., Springer, Berlin 1985, 1987.
- [17] H. Margenau, Philosophical problems concerning the meaning of measurement in physics, Ch. 8 in: Measurement Definitions and Theories (C.W. Churchman and P. Ratoosh, eds.). Wiley, New York 1959.
- [18] J. von Neumann, Mathematical Foundations of Quantum Mechanics. Princeton Univ. Press, Princeton 1955.
- [19] L.E. Reichl, Modern Course in Statistical Physics. Univ. of Texas, 1980.
- [20] C.E. Rickart, General Theory of Banach Algebras. van Nostrand, 1960.

- [21] P. Suppes, D.H. Krantz, R.D. Luce, and A. Tversky, Foundations of Measurements, Vol. 2. Acad. Press, San Diego 1989.
- [22] W.E. Thirring, Course in Mathematical Physics. Vol. 4: Quantum Mechanics of Large Systems. Springer, Berlin 1983.
- [23] J.A. Wheeler and W.H. Zurek (eds.), Quantum Theory and Measurements. Princeton Univ. Press, Princeton 1983.