Probabilistic Foundations of Statistical Mechanics: a Bayesian Approach

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June 28, 2018

Abstract

We examine the fundamental aspects of statistical mechanics, dividing the problem into a discussion purely about probability, which we analyse from a Bayesian standpoint, and a consideration of how the ensuing statistical results can be related to experimental questions. Although mainly concerned with a quantum description of the mechanics, we link to classical equivalent aspects where appropriate. We present in some detail a simplified and tractable version of the calculus of probabilities originally introduced by Cox and use it to set up a convenient and consistent methodology for combining and manipulating probability symbols and subsequently to associate definite and unambiguous numerical magnitudes with appropriate symbols of that calculus where possible. We argue that the existence of a unique maximising probability distribution \( \{ p(j|K) \} \) for states labelled by \( j \) given data \( K \) implies that the corresponding maximal value of the information entropy \( \sigma(\{ p(j|K) \}) = -\sum_j (p_j|K) \ln (p_j|K) \) depends explicitly on the data at equilibrium and on the Hamiltonian of the system. As such, it is a direct measure of our uncertainty about the exact state of the body and can be identified with the traditional thermodynamic entropy. We consider the well known microcanonical, canonical and grand canonical methods and ensure that the fluctuations about mean values are generally minuscule for macroscopic systems before identifying these mean values with experimental observables and thereby connecting to many standard results from thermodynamics. Unexpectedly, we find that it is not generally possible for a quantum process to be both isentropic and reversibly adiabatic. This is in sharp contrast to traditional thermodynamics where it is assumed that isentropic, reversible adiabatic processes can be summoned up on demand and easily realised. By contrast, we find that linear relations between pressures \( P_j \) and energies \( E_j \) are necessary and sufficient conditions for a quasi-static and adiabatic change to be isentropic, but, of course, this relationship only holds for a few especially simple systems, such as the perfect gas, and is not generally true for more complicated systems. By considering the associated entropy increases up to second order in small volume changes we argue that the consequences are in practice negligible.

PACS numbers
1 Introduction

Since the foundational work of Maxwell [1], Boltzmann [2] and Gibbs [3] the field of equilibrium statistical mechanics has evolved into a mature discipline, yet certain aspects of its development and interpretation remain controversial. The strongest version of the ergodic hypothesis (in essence that all phase space states of a system are sampled during a process) held dear by Maxwell and Boltzmann is today generally considered untenable. In his classic textbook, Ma [4] ignores it completely so that it does not even appear in the Index. Boltzmann’s H-theorem, in attempting to explain how a favoured direction of time can emerge from microscopic equations that are themselves time reversible, has probably caused more confusion than enlightenment and raised more questions than it has answered. The arrow of time remains as mysterious today as ever, with explanations in terms of initial conditions only begging the question of how those conditions came into being. Even the idea of ensembles, introduced and used to such exquisite effect by Gibbs, can be viewed as an inessential sop to those who will only accept an interpretation of probability based on frequency of occurrence.

The field is well served by a series of high profile classic, even legendary, textbooks by authors such as Pauli [5], Schrödinger [6], Tolman, [7], Landau and Lifschitz [8], Feynman [9], Kubo [10], Huang [11], Reichl [12] and many, many more. Despite this ocean of high quality material nobody would claim that the last definitive word has been said in this area. We believe that the emergence and growing acceptance of the Bayesian interpretation of probability warrants an attempt to integrate it into a coherent description of equilibrium statistical mechanics, and we aim to take a step in this direction in this article.

We begin by pointing out that the probabilistic and mechanical aspects of the subject are really quite distinct from one another, and that despite the undoubted technical difficulties of the latter it does not present many unsolved questions of principle. Indeed, most of thermodynamics has evolved by avoiding any detailed discussion of the internal mechanics of its systems at all. We therefore concentrate our initial attention on the statistical problem. Although at first sight
the amount of information to be encoded in a probability distribution for a macroscopic system appears overwhelming, in practice we are usually only concerned with reproducible experimental results that depend on just a few parameters. The restricted objective is then to find general relations between some small number of macroscopic parameters and to go on to calculate values of observable quantities using a minimum of additional microscopic information. Most of these results pertain to equilibrium situations, so we discuss this concept, and the related one of irreversibility, in some detail (although touching only briefly on the mechanisms for relaxation to equilibrium). We conclude that the pivotal point is to estimate the probabilities with which the energy eigenstates of the system occur, since this leads to a means of calculating the final expectation values of physical quantities, which may then be compared with their experimental counterparts. We illustrate this conclusion with an early application of microcanonical probabilities, which is to say basically that we take all states within a narrow energy range to be equally likely to occur and so assign them equal probabilities of being the actually occurring state. This is really just Bernoulli’s principle of indifference - a means of reasoning when having incomplete knowledge. In view of the enormous number of accessible states, the success of this postulate must indicate that practically all such states correspond to nearly the same macroscopic properties, and that the statistical averaging is merely preventing the accidental selection of an untypical state. Now in a position to evaluate moments of the distribution, we demonstrate the important point that it only makes sense to identify the calculated mean value with the experimental observable if the standard deviation from the mean is sufficiently small. We do this by considering the pressure exerted by an isolated system, having a measured energy, on its confining walls. We find that the conditions for statistical methods to give sharp numerical results are the same as those required for experimental reproducibility and that the number of accessible states Ω is closely related to the experimental entropy.

Before going any further it is essential to give serious consideration to the question of what we mean by probability. We take the Bayesian view that probability provides a numerical measure of the degree of belief in a proposition based on the available evidence. The major early proponents
of this view were Laplace [13] in the 19\textsuperscript{th} century and Jeffreys [14] in the first half of the 20\textsuperscript{th}. E.T.Jaynes [15] has been a stalwart champion of this approach in the second half of the 20\textsuperscript{th} century. We use probability calculus as a technique for plausible inference and a method for conjectural reasoning, rather than viewing it as an intrinsic measurable property of a given physical event independent of any prior knowledge. We follow Cox [16] in setting up a consistent calculus for combining and manipulating probability symbols. Cox’s work is not widely known, but is entirely accessible to physicists, so we endeavour to explain it as comprehensibly as we can. Cox argues that there is only one possible algebra of probable inference and deduces definite quantitative rules for the combination of probabilities. We hope our explanatory efforts will lead the reader to agree with him in due course. A second major problem in probability theory is to develop a tractable theory of probability assignments. For this we follow Shannon [17] and Jaynes [18] in associating a quantity called the “uncertainty” with a probability distribution over a set of propositions. With a few plausible assumptions about its behaviour and a condition of self-consistency Shannon found a simple, unique function of the probabilities with the desired characteristics to act as this “uncertainty”. In Section 3 we shall sketch his proof before moving on to Jaynes’ use of “uncertainty” as a means of assigning probabilities by what he calls the principle of maximum entropy.

The main idea is to make an impartial assignment of probabilities by maximising the information entropy \( \sigma(\{p_j\}) = -\sum_j p_j \ln(p_j) \), subject to the constraints implied by the data \( K \) and the normalisation condition. Mean values of observables may then be calculated for comparison with experimental measurements. This function \( \sigma_{\text{max}}(\{p_j|K\}) \) possesses all the properties of the thermodynamic entropy \( S \), and we aim to identify it as such, in suitable units. In particular, this requires that we show it to be an extensive function of state, defined for equilibrium conditions, that does not decrease in adiabatic processes and is related experimentally to heat and temperature. We address these questions in Section 4.

The identification of the theoretical quantity \( \sigma_{\text{max}} \) with the phenomenological entropy \( S \) simplifies the development of statistical mechanics. The absolute temperature \( T \) can be then be
introduced into the formalism via the traditional thermodynamical arguments involving the second law. In fact, $T$ can be derived from theory using the relation $\frac{\partial \sigma_{\text{max}}}{\partial E} = \frac{1}{k_B T}$. This requires an explanation of how to calculate the absolute maximum of the information entropy, and the associated probability distribution in terms of the assumed data. This requires a consideration of how to apply a constrained maximisation and how to ascertain that it is indeed the globally largest maximum achievable. In section 5 we will examine this question within the contexts of the traditional microcanonical, canonical and grand canonical methods where only probability is constrained to be normalised, then the mean energy is constrained to a certain value and finally the mean particle number is constrained to a given value. Lagrange multipliers are introduced to handle these calculations and are themselves found to have important physical significance, being related to the equilibrium temperature and chemical potential. We will touch briefly on the third law and the interpretation of negative temperatures, but do not go deeply into these areas since they are more specialised than our current scope warrants.

With the identifications mentioned above in place, we are in a position to derive equations relating the macroscopic and experimentally accessible functions of state to quantities derived by probabilistic methods from the microscopic structure and equilibrium data. In many cases, these are simply differently focused derivations of already well known relations. However, there is one tantalising surprise requiring deeper investigation, concerning the question of whether quasi-static and reversible adiabatic processes are also necessarily isentropic. Such processes are easily defined in thermodynamics, making up essential legs of a Carnot cycle, for example, and are assumed always to be possible. Nevertheless, it is not clear that, for an arbitrary system, their existence is compatible with quantum mechanics and our interpretation of entropy as maximised uncertainty. In section 6 we show that such processes, requiring the entropy to remain constant, are only possible if the energy eigenspectrum at the end is uniformly expanded or compressed with respect to the initial eigenspectrum in the ratio of the final to initial temperatures. This can happen for some very simple, idealised systems such as the perfect gas, but cannot be achieved more generally. In fact, we show that it is equivalent to requiring the correlation coefficient between
energy and pressure deviations to vanish, which in turn requires \( P_j = aE_j + b \) (where \( a \) and \( b \) are constants) for all states \( j \), which is a very special restriction unlikely to be obeyed by any real systems. We discuss this surprise more thoroughly and resolve the apparent discrepancy between thermodynamics and statistical mechanics at the end of section 6,
2 Physics and probability

2.1 Separation of problems

There are two outstanding conceptual difficulties in the study of statistical mechanics. The first is to understand why the ideas of probability are needed at all, and the second is to see why the statistical methods which have been invented can ever give clear-cut answers to experimental questions. It should be firmly grasped at the outset that the probabilistic and mechanical aspects of the subject are quite distinct and that the statistical problem can be solved completely once and for all. The application of this solution to real physical systems usually involves great technical difficulties having to do with the mechanics, but there are few questions of principle left to worry about. Most often we have in the end to be content with rather drastic approximations or model assumptions when trying to predict and understand actual experimental observations.

On the other hand it is frequently possible to understand how various observables of a system are related to each other without using any specific knowledge of the internal mechanics. This is the subject matter of thermodynamics, which relies heavily on the non-mechanical notions of entropy and temperature. The implication is that these latter concepts are fundamentally statistical in character and that the basic laws of thermodynamics follow naturally from considerations of probability. A demonstration of the truth of these statements is an important secondary aim of statistical mechanics.

The typical problem in statistical mechanics is to elucidate the measurable and reproducible properties of a macroscopic system. In principle, mechanics alone should suffice. To see what is involved, consider in outline how a calculation of physical observables might conceivably be attempted using either classical mechanics or quantum mechanics. The methods employed in these two theories are very different, but the logical structure of the two types of calculation is the same. Corresponding steps in the classical and quantum approaches can be set out for comparison as follows:
Table 1: Classical and Quantum Correspondence

| Specification of system | CLASSICAL MECHANICS | QUANTUM MECHANICS |
|-------------------------|---------------------|-------------------|
| Hamiltonian function    | $H = H(\{x_i, p_i\}, t)$ | Hamiltonian operator $\hat{H} = \hat{H}(\{\hat{x}_i, \hat{p}_i\}, t)$ |
| Initial state (at time $t = 0$) | Canonical variables $\{x_i(0), p_i(0)\}$ | State function $\Psi(\{x_i\}, t = 0)$ |
| Equations of motion     | Hamilton’s equations $\dot{x}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial x_i}$ | Schrödinger equation $\dot{\Psi} = i\hbar \frac{\partial \Psi}{\partial t}$ |
| Final state (at time $t$) | Evolved variables $\{x_i(t), p_i(t)\}$ | Evolved state $\Psi(\{x_i\}, t)$ |
| Observable property     | Phase function $Q(\{x_i(t), p_i(t)\})$ | Expectation value $\langle \Psi(t) | \hat{Q} | \Psi(t) \rangle$ |

These familiar expressions need only a little in the way of explanatory comment. The specification of the nature of the system is considered complete when we have enough information to construct the Hamiltonian function or operator, which is in most examples an expression for the energy. This Hamiltonian may have an explicit time dependence arising from variable external forces applied to the system. To start the calculation it is also necessary to know the initial state. This is specified classically as the initial position, in a many-dimensional phase space, of the point representing the system. In quantum theory the state-vector at time $t = 0$ is needed.

The equations of motion in both theories are of first order in time and hence can, in principle, be integrated to give the state of the system at any later time $t > 0$. Finally, the evolved value of an observable may be computed from the variables in classical mechanics by finding the magnitude of the appropriate phase function. The corresponding quantity in quantum mechanics is estimated as the expectation value of a definite operator with respect to the evolved final state-vector.

Since these operations all seem perfectly well defined the question arises as to why statistical theory is needed. One occasionally suggested reason is that the equations of motion are so impossibly complicated that the introduction of probability considerations will somehow enable us to avoid solving them. The dynamical equations are indeed almost always intractably difficult; however, they can not be simplified by probability arguments. In many applications of statistical
mechanics it is in fact possible to dispense with the equations of motion entirely, but the reasons for this have nothing to do with probability theory per se; and in any serious calculation there will still usually be a non-trivial mathematical problem of pure mechanics to be faced squarely.

The true situation is that any approach using mechanics only is bound to be an empty exercise since the information necessary to define the initial state is never available. Setting up a classical initial state would require knowledge of something of the order of $10^{23}$ pairs of canonically conjugate variables \( \{x_i(0), p_i(0)\} \); a similar amount of data in the form of quantum numbers would be needed to specify an initial quantum state \( \Psi(t = 0) \). But the actual knowledge available usually consists of the values of just a few, say two or three, macroscopic observables of the system, and we are forced to guess what state occurs on the basis of this very slender data. It is at this point that probability and statistics enter our subject since these are the tools for informed guesswork. Still, it certainly appears as if the problem is absurdly underdetermined. Any guesses we could possibly make must have an extremely small probability of being correct and it is at first sight miraculous that firm predictions of other observables can be attempted.

Before proceeding to technical details it is perhaps worthwhile to give a rough preliminary answer to the question of how it is possible for our crude guesses to be useful, based as they are on such laughably small amounts of information. The clue is that we choose to record in experimental work only the observationally reproducible results and relations. Hence if it is true experimentally that measurement of just a few parameters of a system suffices for accurate and reproducible estimates of other measurable quantities, then all the fine details of the exact state of the system must be irrelevant.

What is needed theoretically is some highly efficient machinery for bypassing all the redundant details and it is precisely such a beautiful technique that is provided by the general theory of probabilistic inference. We shall apply this method almost exclusively in the context of the quantum mechanics of discrete states. A corresponding conceptual framework can be developed in connection with classical mechanics, but it is much harder to justify and understand; it is also basically unnecessary, since the characteristic classical expressions can usually be deduced
straightforwardly from the quantum results.

The sorts of reproducible information about a system that are practically obtainable can be classified into the three main types mentioned below, though we do not attempt to give an exhaustive list of examples in each category.

- (a) Macroscopic Internal Parameters: including such quantities as the total energy (measured relative to the energy of an arbitrary reference state), the total mass of each constituent, the pressure exerted on the retaining walls, possible electromagnetic moments and various kinds of mechanical strains in the material. Something may also be known about the previous internal history.

- (b) Macroscopic External Parameters: which generally define the environment of the system; whether, for example, it is confined in some definite volume, is acted upon by force fields and mechanical stresses, or is placed in contact with another body with which it can exchange energy or matter. A record of previous manipulations may also be available.

- (c) Microscopic Specification: comprising a knowledge of the kinds and numbers of atoms in a system, with their masses, spins, magnetic moments, spectra, mutual interactions and spatial arrangements, together with the forces acting on them.

Our object is first to establish general relationships between the macroscopic parameters listed under (a) and (b) above (that is, to derive thermodynamics); and second to calculate definite values for the observables using the microscopic information (this of course goes beyond thermodynamics).

2.2 Relaxation to equilibrium

The main accepted results in thermodynamics and statistical mechanics refer to a special condition of systems called equilibrium, and the next order of business is to discuss this important and slippery concept. A related and controversial topic is irreversibility, the indisputable tendency for systems to end up in the condition of equilibrium even though other behaviour is not forbidden
by the laws of mechanics.

The basic experimental fact is that if a macroscopic body is isolated from external influences, except for the presence of static fields and stresses, and it is left to itself for long enough, then its global observable properties will eventually cease to change. The time taken to reach this apparently stationary condition may be fractions of a second or many years, but some period of aging is generally necessary. Furthermore, for the same kind and size of system under the same external conditions, the observed macroscopic quantities have the same final values when equilibrium is reached, which is to say that the results are reproducible. Restricting attention to such a static situation will clearly simplify matters enormously since the equations of motion can be discarded. The crucial point is that when our information no longer changes with time any guess as to what microscopic quantum state actually obtains should also be time independent. Once we have assigned probabilities to the possible states on the basis of some measurements, we can proceed immediately to the final step of estimating observables by means of expectation values. Hence the only conceptual problem left is how to guess the likely states.

These simplifications occur only for the particular global parameters that we have used in judging whether systematic changes in the body have stopped. If we make measurements on too fine a scale in space and time, as for instance rapidly repeated observations of the number of particles in a small part of the system, the results may well fluctuate in time in an unpredictable way. It can happen that the patterns of fluctuation themselves have static and reproducible features, but a detailed treatment of noise spectra and similar topics is outside our scope.

The further questions of why systems relax towards equilibrium and how to calculate the rates at which they do so after some disturbance are also difficult problems. We can, if we like, just take the existence of effective equilibrium situations as a brute fact of nature, and try to describe such conditions, while at the same time hoping to discover how the different equilibria are related. But it is useful and illuminating to discuss briefly the origin of the time dependent relaxation and fluctuation phenomena.

Consider then an isolated system prepared at time \( t = 0 \). It will have a definite Hamiltonian
operator \( \hat{H} \) and a definite state vector \( |\Psi(t)\rangle \) obeying the Schrödinger equation

\[
\hat{H}|\Psi(t)\rangle = i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t}.
\]

(1)

We take the initial state to be normalized by \( \langle \Psi(0)|\Psi(0)\rangle = 1 \) and it then follows easily from the Schrödinger equation that the state remains normalized at later times, i.e. \( \langle \Psi(t)|\Psi(t)\rangle = 1 \) for \( t > 0 \). Typically, the system will have no particular rotational or translational symmetries, but there always exists at least one other constant of the motion apart from the normalization, namely the expectation value of the total energy:

\[
\langle E \rangle_t = \langle \Psi(t)|\hat{H}|\Psi(t)\rangle = \text{constant}.
\]

(2)

This also follows directly from the Schrödinger equation but is easier to understand if we make use of the special solutions of that equation represented by:

\[
|\Psi_j(t)\rangle = |\psi_j\rangle \exp\left(-iE_j t/\hbar\right),
\]

(3)

where the \( |\psi_j\rangle \) satisfy the time-independent equations

\[
\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle,
\]

(4)

and

\[
\langle \psi_j|\psi_k\rangle = \delta_{jk},
\]

(5)

A general normalized state function may be written as a linear combination of these energy eigenstates in the form:

\[
|\Psi(t)\rangle = \sum_j a_j|\psi_j\rangle \exp\left(-iE_j t/\hbar\right)
\]

(6)

where \( \sum |a_j|^2 = 1 \). Hence we have easily that

\[
\langle \Psi(t)|\hat{H}|\Psi(t)\rangle = \sum_{jk} a_j^* a_k \langle \psi_j|\hat{H}|\psi_k\rangle \exp\left(i(E_j - E_k)t/\hbar\right)
\]

\[
= \sum_{jk} a_j^* a_k E_k \langle \psi_j|\psi_k\rangle \exp\left(i(E_j - E_k)t/\hbar\right)
\]

\[
= \sum_j |a_j|^2 E_j = \text{constant}
\]

(7)
If some other observable corresponds to an operator $\hat{C}$ which commutes with $\hat{H}$ then the energy eigenstates may be chosen to be simultaneous eigenstates of $\hat{C}$, and a similar argument shows that $\langle C \rangle_t = \langle \Psi(t) | \hat{C} | \Psi(t) \rangle$ is also a constant of the motion. Note that these results depend only on the system being isolated and not on any assumed condition of equilibrium.

When an observable has an operator $\hat{Q}$ which does not commute with $\hat{H}$ it is a little harder to see how it could eventually come to have an almost constant expectation value. For in this case the energy eigenstates can not be simultaneous eigenstates of $\hat{Q}$ and we are left with the general expression for $\langle Q \rangle_t$ given by

$$\langle \Psi(t) | \hat{Q} | \Psi(t) \rangle = \sum_{jk} a^*_j a_k \langle \psi_j | \hat{Q} | \psi_k \rangle \exp \left( i(E_j - E_k)t/\hbar \right)$$

which contains a constant part and a term depending on time.

Now suppose that the system is prepared at $t = 0$ in some special non-equilibrium condition such that $\langle Q \rangle_{t=0}$ deviates appreciably from the constant part of $\langle Q \rangle_t$. This non-negligible deviation is represented by $\sum_{j \neq k} a^*_j a_k \langle \psi_j | \hat{Q} | \psi_k \rangle$, the initial value of the time dependent part of $\langle Q \rangle_t$. Provided that the various energy differences are largely incommensurate, the individual terms of the time dependent sum will thereafter get out of phase with each other and stay out of phase indefinitely. If in addition the series is not dominated by just a few large terms it is intuitively plausible that as time goes on the initial coherence will be destroyed. That is, it becomes less and less likely that the numerous small terms, with effectively random phases, will add up to give an appreciable contribution. Thus if we wait long enough only the constant part $\sum_j |a_j|^2 \langle \psi_j | \hat{Q} | \psi_j \rangle$ of the general expression for $\langle Q \rangle_t$ survives. It is certainly possible that some partial restorations of coherence will occasionally happen, but for global properties of a system they are so small as to be detectable only with difficulty, and they are in any case fundamentally irreproducible and unpredictable in unique detail, such as experiments on spin-echoes \[19\], which demonstrate spectacular atomic memory phenomena; but in general it remains true that our best estimate of the value of an observable in the long term is given by the constant part of $\langle Q \rangle_t$. 

\[13\]
This dephasing argument, though extremely qualitative, contains the essence of the matter and we see roughly the mechanism for relaxation to equilibrium. At the same time we understand that a quantity which is not a constant of the motion will always, in principle, show fine time-dependent fluctuations about its equilibrium value. Actually, for discrete quantum states, the expectation $\langle \hat{Q} \rangle_t$ is quasi-periodic, which means that it will eventually return arbitrarily closely to its initial value; but for most macroscopic observables the relevant recurrence time is enormously long compared with all feasible observation times. Thus the apparently irreversible nature of relaxation processes in an isolated body is to some extent an illusion. However, for gross collective motions in such a system, which are always observed to die out ultimately, it is a most convincing one.

Our simplified discussion has a bonus in that it strongly suggests that the central concern of equilibrium statistical mechanics is to estimate the probabilities with which the various energy eigenstates occur, for then the final expectation values of physical quantities are computable. The remaining mechanical part of the calculation reduces to the construction and enumeration of the allowed energy states and the evaluation of matrix elements of suitable operators. What is not so clear from the above is why the same system may reach the same reproducible equilibrium condition from a wide range of different initial states. The quantities $\sum_j |a_j|^2$ appearing in the formulae are, of course, interpreted as the probabilities for finding the energy states $|\psi_j\rangle$, given that the actual state is $|\Psi(t)\rangle$, and they obviously depend on exactly what the state vector is. An additional difficulty is that we never really know what $|\Psi(t)\rangle$ occurs, so this must also be guessed before the quantum probabilities $\sum_j |a_j|^2$ are even calculable. Thus there is a second level of probability to be compounded with the first.

The way out is to recall that these compounded probabilities will in the end have to be assigned directly from a knowledge of the observed properties of the final equilibrium state. In particular a measurement of the total energy turns out to be of great utility for this purpose, and for an isolated system the final energy expectation value is necessarily the same as that of the initial state, whatever that may be. We therefore conclude tentatively that all initial conditions which
lead to the same given final equilibrium must imply state vectors $|\Psi(t)\rangle$ with similar probability distributions for the energy eigenstates appearing in them. Discrimination between the state vectors corresponding to the great variety of possible non-equilibrium initial states depends on the phase relations among the terms of their eigenfunction expansions. As we have seen, it is likely that these phase relations become effectively washed out when equilibrium is reached. The last link in the argument is that the energy eigenstates most likely to occur, compatibly with a given total energy, must almost all imply essentially the same set of expectation values for other macroscopic quantities. If it were not so, the equilibrium properties would not be reproducibly related or have sharply reproducible magnitudes.

Conversely, this suggests that knowledge of the equilibrium values of properties other than the energy may be sufficient for the assignment of probability distributions, and hence make possible the prediction of the remaining macroscopic observables, including the energy expectation value itself. Thus the validity of the above remarks does not depend in any essential way on the supposition that we have measured the energy directly.

### 2.3 Microcanonical probabilities

We delay a full exposition of how to assign probabilities until some necessary theory has been developed in the next section. However, we can with profit consider an important special case in order to form some idea of the kind of problem to be solved. The method has the drawback of being rather artificial, but is valuable because the required probabilities are obvious to common sense.

Here and in later treatments of an isolated body we assume that enough is known about the environment and constitution of the system that its Hamiltonian can be written down, at least approximately. This is sufficient data, in principle, to derive its possible energy eigenstates and eigenvalues by solution of the time-independent Schrödinger equation

$$\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle,$$

where the symbol $j$ stands for all the labels necessary to specify the state completely.
Now suppose that an isolated system has reached a condition of equilibrium and that its internal energy has been measured. In practice this energy is determined relative to that of some equilibrium reference state by doing macroscopically measurable amounts of work on the body. The work is performed by altering the applied mechanical stresses or fields in a controllable way and care is taken that the body is not otherwise affected by the environment. Specifically, no part of the resultant energy change can be attributed to the uncontrolled random perturbations called heat transfer. Under these conditions we can assign an internal energy to a given equilibrium state by direct experiment. We have, of course, assumed the law of energy conservation so that the measured external work corresponds to an equal amount of energy gained by the body.

According to the rules of quantum mechanics, a measurement of the energy results in the state of the body becoming an eigenstate of energy, an example of the well-known “collapse of the wavepacket”. The state vector subsequently has the form

$$|\Psi_j(t)\rangle = |\psi_j\rangle \exp(-iE_j t/\hbar),$$

for some $j$, and the constant energy of the system is given by

$$E_j = \langle \Psi(t)|\hat{H}|\Psi(t)\rangle = \langle \psi_j|\hat{H}|\psi_j\rangle,$$

since the harmonic time factors cancel out. Any other observable $Q$ for an isolated system will correspond to an operator $\hat{Q}$ independent of time and our estimate for its magnitude can be taken as the similarly constant expectation value

$$\langle Q \rangle_j = \langle \Psi(t)|\hat{Q}|\Psi(t)\rangle = \langle \psi_j|\hat{Q}|\psi_j\rangle.$$ (12)

The quantum probabilities $|a_j|^2$ of the last subsection are no longer needed, but for two reasons this is not the whole story. One reason is that the eigenstates may be degenerate, which means that there may be many states $|\psi_j\rangle$ belonging to the energy $E_j$; the other is that there will inevitably be some experimental error in the measurement of the energy so that the exact value of $E_j$ is not known. Since our knowledge is not sufficient to pin down the exact state, there still appears to be considerable uncertainty left in our estimates for other observables $Q$, even apart
from the spread of values implied by quantum theory when the operators $\hat{Q}$ do not commute with $\hat{H}$. Clearly we need to assign probabilities to the eigenstates $|\psi_j\rangle$ which could occur consistently with the knowledge we do in practice obtain.

Let us therefore assume as our basic information that the energy has been definitely observed to lie somewhere between a fixed energy $E$ and another fixed energy $E + \Delta E$, where $\Delta E$ is small ($\Delta E \ll E$). Equivalently

$$E < E_j < E + \Delta E.$$

Any state $|\psi_j\rangle$ with an energy $E_j$ obeying these inequalities will be called accessible, and we define a quantity:

$$\Omega = \text{The Number of Accessible States}.$$ 

It is also convenient to let the labels $j$ of these states range over the values $j = 1 \rightarrow \Omega$. The word accessible is used for historical reasons and there is no implication that the system will eventually visit every such state. It means only that our knowledge is consistent with any one of them being the actual state, but that we do not know which one occurs.

Probabilities for the accessible states must be assigned in the light of all available information. This includes the above energy condition and it is also relevant that the states form an exhaustive and mutually exclusive set of possibilities. Exhaustive means that at least one of the $\Omega$ states must occur, which is true by hypothesis. Mutual exclusion signifies that at most one of the $\Omega$ states is the actual state of the system. This follows from the orthogonality of eigenstates of different energy together with the hitherto tacit assumption that the independent states of a degenerate energy level have also been chosen to be orthogonal, as is always possible. For if the energy state $|\psi_j\rangle$ occurs then the condition $\langle \psi_k | \psi_j \rangle = 0$ definitely excludes the possibility of finding any other state $|\psi_k\rangle$. Thus we know that one, and only one, of the $\Omega$ accessible eigenstates must be present as a result of the energy measurement, but our information gives no further help in choosing the right one. As far as we can see, none of the possible states is picked out as being more likely than any other. We must therefore at this point resort to reasonable guesswork and make an unadorned postulate. A plausible statistical theory can be set up on the following
• **Basic Hypothesis:** Given that an isolated system has an energy between $E$ and $E + \Delta E$, every one of its energy eigenstates $|\psi_j\rangle$, $j = 1 \rightarrow \Omega$, with energy eigenvalue $E_j$ lying in that interval, has the same probability of being the actually occurring state.

To apply this, let the probability for the state $|\psi_j\rangle$ be $p_j$. Then the total probability for occurrence of an accessible state must be unity and all the $p_j$ are equal. The two conditions

$$\sum_j p_j = 1 \quad \text{and} \quad p_j = p_k \quad \forall \; j, k$$

lead easily to the probability assignments:

$$p_j = \frac{1}{\Omega} \quad \text{if} \quad E < E_j < E + \Delta E$$

$$= 0 \quad \text{otherwise},$$

and we have derived what is called the Microcanonical Distribution.

Averages are now defined by expressions of the form

$$\bar{X} = \sum_j p_j \langle X \rangle_j, \quad j = 1 \rightarrow \Omega,$$

so that our final estimates for the energy and other observables are

$$\bar{E} = \sum_j \frac{E_j}{\Omega} \quad \text{and}$$

$$\bar{Q} = \sum_j \frac{\langle \psi_j | \hat{Q} | \psi_j \rangle}{\Omega}.$$  

It is obvious from these equations that $\bar{E}$ must lie somewhere between $E$ and $E + \Delta E$, as we already knew; but it is not at all obvious that $\bar{Q}$ will also have well-defined limits. Indeed, as remarked earlier, such an expression for the estimated value of an observable $Q$ will be useful only if almost all states $|\psi_j\rangle$ compatible with our information yield very similar expectation values for $\hat{Q}$. But before discussing this vital point further it is useful to make some comments on the Basic Hypothesis.

The bald postulate announced above has been called the “Principle of Indifference” or “Insufficient Reason” on the grounds that the information available provides no reason to prefer any one
of the allowed possibilities over any other. It is usually attributed to Bernoulli and is discussed at length by Keynes. Some such principle is clearly required, in order to make progress, but the formulation just given has a negative sound to it. To emphasize its positive rôle in the theory, it has been suggested that it should rather be called a “Principle of Consistency”, since it would certainly seem inconsistent to assign greater probability to some subset of the accessible states if the data we have indicate no compelling reason to do so.

It may be objected that some of the states may really be more probable than others; but this implies a view of the concept of probability different from the one adopted here. Our view is basically that probability is an encoding of our knowledge of possibilities, so that it appears at first sight as somewhat subjective and capricious. Objectivity is restored if we insist that anyone with the same data should arrive at the same probability assignments. We discuss these things more fully in the next section, in which the above “Principle of Consistency” will emerge as just a special case of a more powerful algorithm. This more general principle applies even when there is reason to prefer some possibilities over others.

Returning now to the special assumptions of this subsection, it is important to realise that our probability postulate (or Basic Hypothesis) is not a physical principle, but only a way of reasoning in the face of uncertainty, and hence requires no justification from physics. The system is not in a probability distribution but in some definite state that we do not happen to know. Thus we have to form an opinion about which state really occurs and this is most consistently represented by the assumption of equal probabilities for the states permitted by the data. If we want to do any better than this then more information must be acquired.

Obvious though all this may appear, we emphasize it because many attempts have been made to justify the principle by physical arguments. The idea is that the system, perhaps under the influence of tiny but uncontrollable perturbations, continually makes transitions between its various eigenstates, so that it spends an equal amount of time in each possible state. There, it is implied, since an observation takes a finite time, a time-averaged observed value can be calculated as an average over the ensemble of accessible system states at a fixed time, each occurring with equal
probability. This sounds plausible but has never been proved even for averages over indefinitely long times, let alone for the quite short times involved in typical experiments. Very much more to the point, it is easy to see that only a vanishingly small fraction of the accessible states could be sampled in any reasonable observation time.

For if we assume, conservatively, that each of the $3 \times 10^{22}$ degrees of freedom of even a quite moderately sized body could have only two likely quantum number values at equilibrium, then the number of possible states would be $2^{(3 \times 10^{22})} \approx 10^{(10^{22})}$. Assuming further that the transition rate for each degree of freedom reaches as high as $10^{20}$ per second (thus approaching nuclear rates [22]), then the transition rate for the whole body would be of the order of $10^{42}$ per second. The time required to visit each state even once would then be $10^{(10^{22} - 42)} \approx 10^{(10^{22})}$ seconds and this is so long that it hardly matters whether we express it in seconds or in units of the age of the universe, which is a mere $10^{17}$ seconds. The time-averaging suggestion is seen to be quite implausible.

The real problem to be understood is why our statistical averaging over the almost incomprehensibly huge number of accessible states leads to values of observables in agreement with experiment, even though the system will never actually be in the overwhelming majority of such states. The only conceivable reason for the practical success of our postulate is that virtually every accessible state has nearly the same macroscopic properties and the averaging is necessary merely to avoid picking out an untypical state accidentally.

2.4 Estimation of observables

We now investigate in a little more detail how the estimate

$$\bar{Q} = \sum_j \frac{\langle \psi_j | \hat{Q} | \psi_j \rangle}{\Omega}$$

for the value of an observable could be useful. What we require is that any value likely to be found as a result of measurement should be near to the number $\bar{Q}$, i.e. that the magnitude $|\Delta Q|$ of the observed deviation from $\bar{Q}$ should virtually always satisfy the relation

$$\frac{|\Delta Q|}{Q} \ll 1.$$
In principle, the various quantum expectation values $\langle \psi_j | \hat{Q} | \psi_j \rangle$ could be wildly different from each other and, although the average $\bar{Q}$ would then still be a definite number, actual observations would show a large spread of results about the mean. Sharply reproducible results can be expected only if it is possible to demonstrate that

$$\langle \psi_j | \hat{Q} | \psi_j \rangle \approx \langle \psi_k | \hat{Q} | \psi_k \rangle$$

for nearly all arbitrarily selected pairs of accessible states $|\psi_j\rangle$ and $|\psi_k\rangle$, and in addition that these matrix elements themselves represent sharp quantum predictions given the energy states involved. Obviously it is impossible to give a general proof of such properties and each suggested observable for a particular system must be treated separately. Alternatively we can choose to calculate only those macroscopic quantities which are in fact observed to be reproducible experimentally, for then the conditions mentioned must be satisfied.

As a specific example consider the possibility of estimating the pressure exerted by an isolated system, of measured energy, on its confining walls. We assume that the system always exactly fills the container even when the volume $V$ is varied over some range of values. An important special case of this is a gas contained in a cylinder which is fitted with a movable piston. The parameter $V$ will certainly appear in the defining Hamiltonian operator $\hat{H}$ and it follows that the accessible energy eigenstates and eigenvalues will also in general depend on $V$.

To calculate the pressure $P$, imagine that the system is in a definite state $|\psi_j(V)\rangle$ belonging to energy $E_j(V)$ and that the volume is changed, adiabatically and slowly, by a small amount $\Delta V \ll V$. An adiabatic change is defined as one brought about by adjustment of the force fields or mechanical stresses acting on a body, which remains otherwise isolated from its environment. It is implied that the Hamiltonian changes in a definite way, e.g. $\hat{H}(V) \rightarrow \hat{H}(V + \Delta V)$. By a slow change we mean that the change proceeds so gradually that the system effectively stays at all times in an eigenstate of its gently evolving Hamiltonian. This slowly applied perturbation causes the accessible eigenstate $|\psi_j(V)\rangle$ of $\hat{H}(V)$ to go smoothly and continuously to a corresponding accessible eigenstate $|\psi_j(V + \Delta V)\rangle$ of $\hat{H}(V + \Delta V)$; there are no transitions to other eigenstates,
and the total number of accessible states is unchanged. After these explanations it should be sufficiently clear that in our slow, adiabatic process the work done on the system is equal to the change in its internal energy \( E_j(V) \) and we may write

\[
\Delta E_j \approx \left( \frac{\partial E_j(V)}{\partial V} \right) \Delta V = -P_j \Delta V
\]

(22)

The second equality records the accepted relation between pressure and work done in a small change of volume, and we have at once that the pressure \( P_j \) in state \( |\psi_j\rangle \) is

\[
P_j = -\frac{\partial E_j(V)}{\partial V}.
\]

(23)

The pressure observable may also be written, in conformity with previous expressions, as the expectation value of an operator in the state \( |\psi_j\rangle \). A straightforward exercise in quantum mechanics soon shows that for discrete, normalized, energy eigenstates of \( \hat{H} \) we have

\[
P_j = \left\langle \psi_j \left| -\frac{\partial \hat{H}(V)}{\partial V} \right| \psi_j \right\rangle = -\frac{\partial E_j(V)}{\partial V}.
\]

(24)

A similar theorem holds for any observable whose effective operator can be represented as the derivative of the Hamiltonian \( \hat{H} \) with respect to a parameter. We mention in passing that such operators, and in particular the pressure \( \hat{P} = -\frac{\partial \hat{H}}{\partial V} \), usually do not commute with the Hamiltonian and are therefore not constants of the motion. As explained before, nearly steady expectation values would then be attained only at equilibrium and fluctuations are inevitable.

Our statistical estimate for the equilibrium pressure \( \bar{P} \) is computed by averaging the pressures \( P_j \) over the microcanonical probability distribution appropriate to accessible states:

\[
\bar{P} = \frac{\sum_j P_j}{\Omega} = \left[ \frac{\sum_j \frac{\partial E_j(V)}{\partial V}}{\Omega} \right].
\]

(25)

Now the change envisaged in the definition of pressure in an isolated system was such that the number of accessible states remains constant. Therefore on rearranging, we have

\[
\bar{P} = -\frac{\partial}{\partial V} \left[ \frac{\sum_j E_j}{\Omega} \right] = -\left( \frac{\partial \bar{E}}{\partial V} \right)_{\Omega=\text{constant}}.
\]

(26)

Hence our estimate of the pressure will be good only if the observed energy is a smooth, reproducible function of volume in a slow, adiabatic process, which is very often true experimentally.
On the theoretical side we would have to show that most accessible energy eigenvalues $E_j(V)$ have closely equal derivatives $\frac{\partial E_j(V)}{\partial V}$. Again, this is found to be true in many analytically tractable models. It is certainly true, for example, for a gas of structureless, non-interacting particles over a wide range of internal energy. It will be shown later, for this model, that the pressures are given by $P_j = \frac{2}{3}E_j/V$, from which it follows that

$$\frac{2E}{3V} < \bar{P} < \frac{2(E + \Delta E)}{3V},$$

(27)

implying that the estimated pressure $\bar{P} = \frac{2\bar{E}}{3V}$ will lie between close limits if $\Delta E \ll E$.

In this subsection we have pointed out the basic preconditions for statistical methods to give sharp answers and shown that they are the same as those for experimental reproducibility. The main conclusion is that when we estimate a physical quantity we should at the same time attempt to assess the expected deviations of actual observations from our result, for only then is it possible to judge whether the calculation will provide useful predictions and systematizations of experience.

2.5 Significance of $\Omega$-number

It may seem from the development so far that the quantity $\Omega$, the number of accessible states, is of somewhat secondary importance - a sort of mathematical prop to be discarded eventually. For we have been at pains to emphasize that averaging over the uniform probability distribution of accessible states is reasonable only if most such states have similar macroscopic properties. A closer look soon shows that $\Omega$ is in fact a highly significant function of the data used in its construction. A hint of this appeared already in our general expression for the estimated pressure of an isolated system, which was

$$\bar{P} = -\left(\frac{\partial \bar{E}}{\partial V}\right)_\Omega.$$

(28)

where the derivative is taken with $\Omega$ held constant. This should be compared with the well-known thermodynamical formula for pressure in terms of the volume derivative of the internal energy $\bar{E}$, i.e.

$$\bar{P} = -\left(\frac{\partial \bar{E}}{\partial V}\right)_S.$$

(29)
in which the quantity held constant is the entropy $S$.

There is here a strong suggestion that $\Omega$ is closely related to the experimental entropy. The idea is well founded and we shall eventually present detailed arguments to show that for an isolated system of known internal energy the exact connection has the form

$$S = k_B \ln (\Omega),$$

(30)

where $k_B$ is Boltzmann’s constant. Analogous relations between entropy and purely statistical constructs hold also under other experimental conditions and they provide the fundamental links connecting microscopic mechanics with phenomenological thermodynamics. Although statistical mechanics can be developed without reference to thermodynamics, greater understanding is achieved by extracting such connections as exist, both for their intrinsic interest and in order to get some insight into that other mysterious concept of thermal physics, namely, the temperature.

There is, however, a striking conceptual difficulty in any attempt to identify the apparently distinct notions of experimental entropy and statistical uncertainty. In many accounts entropy appears as a physical property of bodies, as definite as mass or energy, to be measured with laboratory instruments, and admitting no ambiguity apart, perhaps, from an arbitrary additive constant. Statistical uncertainty, as represented here by the number $\Omega$ of macroscopically indistinguishable states, seems by contrast to be much more something to do with our knowledge (or rather, lack of knowledge) of bodies than with any intrinsic physical properties possessed by them. That is, it appears to be in the mind. It is certainly true that the usual entropy $S$ is a peculiar physical quantity, much harder to grasp than others, since it is not conserved like mass and energy, but instead has the strange tendency to increase in spontaneous natural processes. This, of course, parallels the undoubted fact that our uncertainty about the state of a body will increase when some uncontrolled change occurs. We will indeed show later that this type of analogy extends to fine details, in the sense that exact mathematical correlations exist between the behavioural properties of the entropy $S$ and a suitable statistical measure, exemplified here by the expression $\ln(\Omega)$. 
Mathematical analogies alone, however, are not sufficient to guarantee the identity of the underlying concepts, since it sometimes happens that similar mathematical theories can apply to quite unrelated phenomena. A physical postulate is unnecessary in order to link theory and experience in the present instance. A reasonable assumption is that the statistically calculated properties of macroscopic systems will agree with experiment. This goes far beyond what can be rigorously demonstrated by actual calculation and observation; but whenever the mathematical problems can be solved for a realistic model the assumption is convincingly verified. To connect with thermodynamics, a relevant remark is that a great accumulation of experience confirms the utility of entropy for the correlation and understanding of experimental properties of systems.

Some of the mystery surrounding the proposed identification of entropy and uncertainty disappears when we enquire into their functional dependence on observed data. An adequate thermodynamic description of a body is at hand when we know the entropy as a function of the internal parameters. In particular, we may know the volume $V$ of the system and the amount of matter in it, to be represented by the number $N$ of particles, assumed all of one type. Then we require the function

$$S = S[E, V, N],$$

from which many physical predictions may be obtained by differentiation.

There is a tacit assumption here that the above variables are the only relevant ones. But it may happen that the derived predictions do not all agree with experiment. In that case, we do not abandon thermodynamics, but take it as an indication that some other relevant parameter has been overlooked — for instance, the presence of a magnetic field. We then seek more data to determine the dependence of $S$ on this new quantity and so discover many further implied relationships to be checked by observation. The conclusion is that entropy depends very much on what we choose to measure, which means that it embodies our knowledge of the system.

The quantity $\Omega$ defining the probabilities of the microcanonical distribution also depends very much on what we choose to measure and take into account. The Hamiltonian $\hat{H}$ and energy eigenvalues $E_j$, depend parametrically on volume $V$ and particle number $N$ and the accessible
states are by definition those lying in an experimentally determined energy interval. Explicitly:

\[ \Omega = \Omega[E \leq E_j(V,N) \leq E + \Delta E] \]
\[ \approx D[\bar{E}, V, N].\Delta E \]  \hspace{1cm} (32)

The second, approximate, equality expresses \( \Omega \) as the product of the error interval \( \Delta E \) and a function \( D \), the density of states, which represents the number of accessible states, per unit energy, in the vicinity of \( \bar{E} \). Clearly, \( D[\bar{E}, V, N] \) depends on the same kind of data as does \( S \).

The approximate expression for \( \Omega \) in terms of the density of states \( D \) is adequate, for all practical purposes, when \( \Delta E \ll \bar{E} \). If \( \Delta E \) is fixed, and we write

\[ S = k_B \ln (\Omega) = k_B[\ln (D(\bar{E}, V, N)) + \ln (\Delta E)] \]  \hspace{1cm} (33)

as suggested earlier for the isolated system, we see that to predict physical observables, which are derivatives of \( S \) thermodynamically, the required mechanical quantity is the density of states function \( D \). Given this link between thermal and mechanical concepts we see, incidentally, that measurement of \( S \) gives information on the distribution of energy levels in the system.

However, independently of this proposed connection between \( S \) and \( \Omega \) (or equivalently \( D \)), physical observables may be estimated directly from their quantum expectation values in the accessible energy eigenstates, using the probabilities assigned to such states. Now it may well happen that the majority of accessible states, as calculated for given \( V \) and \( N \), in an interval \( \Delta E \) surrounding \( \bar{E} \), have macroscopic properties which do not agree with experimental results. As before, we would not therefore immediately abandon the calculation, but conclude that a relevant parameter in the system Hamiltonian had been overlooked, and that only a subset of the previously determined states is actually accessible under the conditions of the experiment. Thus the effective density of states must be changed, its dependence on the new parameter calculated, and its predictions again probed by observation. The analogy with the experimental use of entropy is confirmed.

What emerges very clearly from all this is that the statistical method is an efficient way of reasoning about the data and its relation to the underlying physics, but is not in itself a physical
theory. We might even claim that the results of statistical mechanics are most useful when they
do not agree with experiment. For then, assuming we have confidence in our theoretical models
and mathematical techniques, we will learn something new.
3 Probability and uncertainty

3.1 What is probability?

We have talked rather loosely about the concept of probability and must now attempt to make the idea sharper. This involves a digression from physics, but a very necessary one, for we wish to divorce the basic notions of probability theory from any dependence on experimental facts. As remarked before, the probabilistic aspects of statistical mechanics are susceptible of a complete treatment independent of the mechanical laws underlying the observed phenomena.

From the earliest days of probability there have been two competing views on its nature. One is that it records the ratio of the number of times a particular type of event occurs to the total number of trials in a statistical experiment. This is called the Frequency Theory. The other is that it encodes by a numerical measure the degree of belief one can reasonably accord to some assertion on the basis of available evidence. This is known as the Bayesian Theory, in which the probability calculus is regarded as a technique for plausible inference. According to the first interpretation, probability is an intrinsic measurable property of physical events independent of what we happen to know. On the other view it is a quantitative way of thinking about suggested propositions even when our knowledge is not sufficient to decide definitely on their truth or falsity. That is, probability is taken to be a method for conjectural reasoning, making consistent use of the relations of partial implication connecting conclusions with given hypotheses.

We hold to the second view as being wider and more generally useful than the first, for it can be applied in situations where statistical testing is inappropriate or impossible. To avoid unnecessary considerations of time ordering, it is also convenient to think of probabilities as being attached to propositions rather than to events. However, if statistical evidence on events is in fact available, and relevant, it may still be incorporated into assessments of probability. Our working hypothesis on the nature of the theory is that it provides sets of numerical codings for the credibilities we may consistently associate with propositions, given relevant background knowledge and particular evidence. In other words all probabilities are conditional and a change in the evidence may well entail a change in the probabilities. Clearly therefore we are not regarding probability as a physical
property of objects or processes but as a representation of our state of knowledge about the world.

The main trouble with this interpretation, in the view of many authors, is that it seems too vague and subjective, while the frequency theory appears definite and not dependent on the idiosyncrasies of individuals. The objection does not hold up on further examination. The notion of probability as an algebra of plausible inference can be made quite adequately sharp, as we shall show, by invoking a criterion of internal consistency. In addition, the apparent subjectivity of degrees of belief can be removed by adopting consistent rules of numerical coding, so that when different people assess the same proposition in the light of the same evidence they arrive at the same number for the probability. The foundation of a satisfactory theory of probability thus requires the solution of two major problems:

- (I) How to set up a convenient and consistent calculus for combining and manipulating probability symbols.

- (II) How to associate definite and unambiguous numerical magnitudes with appropriate symbols of the calculus.

The above questions arise on any view of the subject. Let us consider briefly how they appear in the frequency interpretation. The second one now looks rather trivial since in that theory the probability values are defined directly in terms of numbers of instances in a long series of trials. The catch is that different finite series of trials for the same type of event usually give somewhat different numbers. Thus we are forced to postulate that the relative frequency we require will settle down to a definite ratio in the limit of an infinite number of trials. The finite experiments that we can in reality perform yield only estimates of the assumed intrinsic probabilities, and thus some of the definiteness of the frequency idea begins to evaporate. A formal solution to the first problem can be constructed by defining sample spaces of events and associating probability measures with the various subsets of events in those spaces. Then, by analogy with the observed behaviour of stable relative frequencies, some quantitative axioms for the measures are laid down. But one might reasonably enquire whether the particular axioms chosen are consistent, in the sense that
different ways of doing a calculation will not result in contradictions. It is also pertinent to ask if other sets of axioms can be found which might possibly extend the scope of the theory. The frequency model itself now begins to look decidedly indefinite and arbitrary and we return to our favoured view.

A much more powerful and persuasive approach to the question of how to construct a calculus of probabilities was advanced by R.T.Cox [16], around the middle of the 20th century, but has not yet become standard material in books. On the basis of two highly plausible qualitative assumptions, together with an axiom of consistency, he proved that there is only one possible algebra of probable inference. His argument leads to definite quantitative rules for the combination of probabilities, though their exact form can be changed by purely mathematical transformations. The proof is extremely interesting and will be sketched below. It turns out to be surprisingly easy to understand considering that the main tools employed are the rather unfamiliar ones of symbolic logic and functional equations.

The other part of probability theory, how to choose numerical values for probabilities in a rational way, is not at present a completely solved problem. When we can reasonably show for some situation that there exists a set of exhaustive and mutually exclusive inferences and that our knowledge does not suggest any preferred selections among them, then clearly a principle of indifference can be formulated. The only rational choice is equal probability for each inference, as in our example of the microcanonical description of an isolated body. But, when the conditions for indifference are not satisfied, it is tempting to believe that no general method is possible except to rely on frequency data. If such data are not available the problem of assigning initial probabilities in a calculation becomes acute. However, there does exist a certain class of problems, which includes the questions of statistical mechanics, for which it is possible to develop a useful theory of probability assignments, independent of frequencies.

The central concept of this alternative assignment theory originated in work of C.E.Shannon [17], also around the middle of the 20th century, and its significance for the problem of inference was pointed out by E.T.Jaynes [18] some ten years later. The fundamental idea is to associate with
a probability distribution over a set of propositions a quantity we shall call the Uncertainty. Bear in mind that the probability for a single inference represents our state of partial belief in the truth of the inference, and so implies some degree of uncertainty. To begin with, the concept of the total amount of uncertainty implied by the full set of probabilities is a little vague, but we try to invent a way of representing, by a single number, our overall state of doubt about which proposition is true. If we believe more strongly in some of the possibilities than in others we usually feel less uncertain about the true situation than if our evidence implied that all propositions were equally likely. The problem is to quantify this kind of feeling by an objective measure. By making a few plausible qualitative assumptions about how such a measure of uncertainty should behave, and imposing a condition of self-consistency, Shannon [17] proved that there exists a simple unique function of the probabilities which has the desired characteristics. The argument proceeds by setting up and solving functional equations and the whole method is similar in principle to that used by Cox [16] for deriving the probability calculus itself. In view of the importance of the result we shall outline the proof.

The contribution of Jaynes [18, 21] was to use the Uncertainty function as a tool for assigning probabilities. He proposed that in the absence of sufficient information, statistical or otherwise, for direct evaluation of probabilities, they should be chosen so as to make the Uncertainty an absolute maximum, subject only to the constraints imposed by the evidence we do possess. The underlying idea is to admit that our state of doubt in any situation is limited solely by the amount of relevant data we have acquired. The effect of this procedure is to distribute the total probability as evenly as possible over the allowed inferences, without contradicting the given evidence, and the method emerges as a natural generalisation of the Principle of Indifference. In particular it gives some weight to every proposition not completely ruled out by the data. Such a spreading out of the probability, or hedging of bets, is clearly a desirable feature for any method of inference.
3.2 Algebra of probability

We now intend to show how to derive a consistent calculus for combining probabilities without invoking the idea of frequencies in a series of trials. This is important because the interesting questions in statistical mechanics are not really statistical at all, but concern reasonable expectation. Basically we assume that degrees of belief in various propositions $A$, $B$, etc., or perhaps $\{A_m\}, m = 1 \to M$, may be represented by real numbers on some scale. We also assume that there is some information or evidence available to be used in assessing the truth of a proposition. The statement of this background knowledge will be denoted by $K$. Occasionally the writing of $K$ will be suppressed, but it must always be considered as present. The primitive notion of the credibility of an inference $A$, given evidence $K$, will be symbolised briefly by $(A|K)$.

The measure to be attached to a credibility $(A|K)$ is very vague at this stage, and clearly any function of such a number will also constitute a measure. Instead of using the term probability immediately, let us assume merely the existence of at least one convenient scale, written as a numerical function $\alpha(A|K)$ of the credibility. This number will be called the assessment of $A$ given $K$, and we make it a convention that the stronger the credibility then the larger will be the number $\alpha$. There will always be some element of convention in setting up a scale of assessment, but it is also necessary that any scheme for combining assessments should be consistent with the algebra of propositions.

We shall take it that the propositions $A$, $B$, etc., are statements that can be either true or false, but are never self-contradictory or devoid of meaning, and that to assert $A$ is just to say that $A$ is true. We also introduce below the usual notation for the negation of a proposition and for two distinct ways of combining statements into compound assertions:-

$$\sim A = \text{NOT } A \Rightarrow A \text{ is not true} \quad (34)$$

$$A.B = A \text{ AND } B \Rightarrow \text{Both } A \text{ and } B \text{ are true} \quad (35)$$

$$A \vee B = A \text{ OR } B \Rightarrow A \text{ is true or } B \text{ is true or both of them are true} \quad (36)$$
In what follows brackets are employed to distinguish compound statements which are to be treated as logical units, e.g., \( C \equiv (A.B) \) or \( B \equiv (\sim A) \).

There are a number of simple rules obeyed by the indicated operations and it is possible to set up an axiomatic theory for them. We shall not do this formally since the rules required are obvious transcriptions of common sense. Thus the symbol \( \sim (\sim A) \) just means that it is not true that \( A \) is not true, i.e. \( A \) is true, and we easily see that:

\[
\sim (\sim A) = A
\]  \hspace{1cm} (37)

Similarly, \((A.A)\) means only that \( A \) is asserted twice, which is just to assert \( A \). Hence we obtain the rule:

\[
A.A = A
\]  \hspace{1cm} (38)

In the same sort of way a direct consideration of the ordinary meanings of words enables us, with a little thought, to see the truth of the following relations:

\[
A.B = B.A
\]  \hspace{1cm} (39)

\[
\sim (A \lor B) = (\sim A).(\sim B)
\]  \hspace{1cm} (40)

\[
A.(B.C) = (A.B).C = A.B.C,
\]  \hspace{1cm} (41)

together with the corresponding equations in which the symbols AND and OR are interchanged. Where confusion might arise we shall always spell out the meanings of our equations in full.

Consider now how we could assess the credibility of \((A.B)\) on evidence \( K \). Our belief in the truth of both \( A \) and \( B \) will presumably be conditioned, first, on how strongly we believe in \( B \) given \( K \) and, second, on what credibility can be associated with \( A \) given that both \( B \) and \( K \) are true. In short, the credibility \((A.B|K)\) must depend somehow on the credibilities \((B|K)\) and \((A|B.K)\).

Expressed mathematically, this means that any proposed assessment numbers should satisfy the equation:

\[
\alpha(A.B|K) = F[\alpha(A|B.K), \alpha(B|K)],
\]  \hspace{1cm} (42)

where \( F[x, y] \) is some two-variable function.
This is obviously a very weak assumption, especially when we remember that no specific scale for the assessments has so far been suggested. Yet the function $F$ is not completely indeterminate, since we require internal consistency, which implies that different ways of assessing a credibility should lead to the same assessment number. A useful condition on $F$ is obtained by looking at the conjunction $(A.B.C)$ of three propositions, in the two equivalent forms $(A.B).C$ and $A.(B.C)$. Suppressing $K$ for the moment, we have from the first form that

$$\alpha[(A.B).C] = F[\alpha(A.B|C), \alpha(C)]$$

(43)

$$= F[F[\alpha(A|B.C), \alpha(B|C)], \alpha(C)],$$

(44)

while the same number expressed using the second form leads to

$$\alpha[A.(B.C)] = F[\alpha(A|B.C), \alpha(B.C)]$$

(45)

$$= F[\alpha(A|B.C), F[\alpha(B|C), \alpha(C)]],$$

(46)

Hence, if we write $\alpha(A|B.C) = x$, $\alpha(B|C) = y$ and $\alpha(C) = z$, consistency requires that

$$F[F(x, y), z] = F[x, F(y, z)],$$

(47)

which is a non-trivial functional equation restricting the form of $F$.

It is easily verified that a solution of this equation is expressible by means of an arbitrary, monotonic, one-variable function $G$ as follows:

$$F(x, y) = G^{-1}[G(x)G(y)],$$

(48)

where $G^{-1}$ is the function inverse to $G$. Cox [16] has shown, under rather mild conditions of differentiability and continuity on $F$, that this is the most general solution. A more convenient form for the above results is

$$G[F(x, y)] = G(x)G(y),$$

(49)

This way of writing the solution suggests the definition of another numerical measure of credibility which is related to, but more useful than, the originally assumed function that we called the
assessment. For it is now possible to state that whatever scale we may have selected for the \( \alpha \)-numbers, provided that it represents consistent reasoning, we can always find a function of those numbers, given by

\[
\beta(A|K) = G[\alpha(A|K)], \tag{50}
\]

which obeys a simple multiplicative rule of combination. We shall call this new measure the \textit{believability} of \( A \) given \( K \). Thus, on taking the function \( G \) of both sides of our starting equation (42), we see easily that

\[
G[\alpha(A.B|K)] = G[F[\alpha(A|B.K), \alpha(B|K)]] = G[\alpha(A|B.K)]G[\alpha(B|K)], \tag{51}
\]

so that the rule for believability of conjoined statements on evidence \( K \) reduces to

\[
\beta(A.B|K) = \beta(A|B.K)\beta(B|K), \tag{52}
\]

If we take \( G \) to be monotonically increasing, then our convention, that greater assessment numbers \( \alpha \) correspond to greater credibilities, applies also to the believabilities \( \beta \).

The above remarkable result implies a definite numerical value for the believability to be associated with an inference which is certain on given evidence. Putting \( A = B \), and remembering that \((A.A) = A\), we obtain

\[
\beta(A|K) = \beta(A|A.K)\beta(A|K). \tag{53}
\]

Any proposition \( A \) not contradicted by \( K \) is clearly certain given that \((A.K)\) is true; hence we easily deduce the extreme value

\[
\beta(\text{Certainty}) = 1. \tag{54}
\]

To complete the calculus we need a rule connecting the believabilities of a proposition \( A \) and its negation \((\sim A)\). Again a qualitative hypothesis is sufficient, if we begin to believe more strongly in the truth of some statement then we usually believe less strongly in its denial, which is only to say that we feel that their believabilities are somehow related. In symbols:

\[
\beta(\sim A|K) = f[\beta(A|K)] \tag{55}
\]
and
\[ \beta(A|K) = f[\beta(\sim A|K)], \tag{56} \]

where \( f(x) \) is some one-variable function and the second equation follows from the first on replacing \( A \) by \( \sim A \) and using \( \sim (\sim A) = A \). By putting the first equation into the second and writing \( \beta(A|K) = x \) we see that the function \( f \) must satisfy the relation
\[ f[f(x)] = x. \tag{57} \]

This is not a very restrictive condition and another one must be found by a further argument based on consistency requirements. One possibility is to consider two different ways of evaluating the number \( \beta((\sim A).B|K) \). We use our hypothesis on negation together with the multiplicative rule for the believability of conjoined propositions which was derived above. The symbol \( K \) for the background evidence will be dropped temporarily in order to simplify the equations, but is still understood to be present. In particular, we need to assume in the following manipulations that the propositions and their negations are not impossible given evidence \( K \). With this proviso we may write the sequence of relations:
\[
\beta((\sim A).B) = \beta(\sim A|B)\beta(B)
\]
\[
= f[\beta(A|B)]\beta(B)
\]
\[
= f \left[ \frac{\beta(A|B)\beta(B)}{\beta(B)} \right] \beta(B)
\]
\[
= f \left[ \frac{\beta(A|B)}{\beta(B)} \right] \beta(B). \tag{58}
\]

Next consider the expression \( B.(\sim (A.B)) \). This asserts that \( B \) is true and that simultaneously not both of \( A \) and \( B \) are true. This is the same as to say that \( (\sim A) \) is true and that \( B \) is also true, i.e. to assert \( ((\sim A).B) \). Thus we get the logical equation
\[ (\sim A).B = B.(\sim (A.B)), \tag{59} \]

from which we obtain the corresponding believability relation
\[ \beta(((\sim A).B) = \beta(B.(\sim (A.B))). \tag{60} \]
Now it is easy to see that the second compound proposition is actually of the same form as the first, if we think of \((\sim A)\) being replaced by \(B\) and \(B\) being replaced by \(\sim (A.B)\). On repeating the above sequence of relations with these replacements we soon find that

\[
\beta(B.(\sim (A.B))) = f \left[ \frac{\beta((\sim B).(\sim (A.B)))}{\beta(\sim (A.B))} \right] \beta(\sim (A.B))
\]  

(61)

But with a little thought, it is clear that to assert \((\sim B).(\sim (A.B))\) is to assert \(\sim B\) alone since it states that \(B\) is not true and that not both of \(A\) and \(B\) are true, which is always true if \((\sim B)\) is, independently of the truth of \(A\). In terms of believabilities therefore

\[
\beta((\sim B).(\sim (A.B))) = \beta(\sim B),
\]

(62)

and our chain of equations establishes that

\[
f \left[ \frac{\beta(A.B)}{\beta(B)} \right] \beta(B) = f \left[ \frac{\beta(\sim B)}{\beta(\sim (A.B))} \right] \beta(\sim (A.B)).
\]

(63)

Finally, we write \(\beta(B) = x\), so that \(\beta(\sim B) = f(x)\), and \(\beta(\sim (A.B)) = y\), implying \(\beta(A.B) = f(y)\), to obtain the equation

\[
xf \left[ \frac{f(y)}{x} \right] = yf \left[ \frac{f(x)}{y} \right]
\]

(64)

as an interestingly symmetric condition to be satisfied by the function \(f\) along with the first consistency relation \((57)\ f[f(x)] = x\).

Cox [16] has proved that the unique general solution of these two equations, again under mild assumptions of differentiability, is

\[
f(x) = [1 - x^m]^{1/m},
\]

(65)

where \(m\) is a non-zero real number. A more useful form for the result is

\[
(f(x))^m = [1 - x^m].
\]

(66)

With this theorem to hand it is now possible to define a particularly convenient final scale for a measure of credibility by writing

\[
p(A|K) = \beta^m(A|K), \quad m > 0.
\]

(67)
Since our previous equations imply that

\[ \beta^m(A.B|K) = \beta^m(A|B.K) \beta^m(B|K) \]  

(68)

and

\[ \beta^m(\sim A|K) = (f[\beta(A|K)])^m = 1 - \beta^m(A|K), \]  

(69)

we see that the numbers \( p(A|K) \), now called \textit{probabilities}, satisfy the very simple combination rules

\[ p(A.B|K) = p(A|B.K) p(B|K) \]  

(70)

and

\[ p(\sim A|K) = 1 - p(A|K), \]  

(71)

while the choice \( m > 0 \) ensures, in line with our previous conventions, that stronger credibility corresponds to greater probability.

The last two relations constitute one form of the usually accepted rules of probability calculus and we have demonstrated, independently of any considerations of frequencies, that they are equivalent to all possible \textit{consistent} versions of such a calculus. Numerical values for the \( p(A|K) \) are fixed, so far, only at the extremes of certainty and impossibility since \( p = \beta^m \) yields

\[ p(\text{Certainty}) = 1 \]  

(72)

and the probability of an impossible proposition follows easily. For if \( A \) is certain on given evidence then \( (\sim A) \) is impossible on the same evidence and hence, by the second rule shows

\[ p(\text{Impossibility}) = 0. \]  

(73)

Notice, however, that the rules tell us nothing about how to assign probabilities for propositions which are neither certain nor impossible on the given evidence, except that they should be chosen between zero and unity to be consistent with our convention that probability is an increasing function of credibility. It is therefore clear that to address the problem of \textit{assigning} probabilities we have to go beyond the algebraic rules for manipulating and combining them. The assignment
problem of probability theory is indeed hardly mentioned at all in most accounts of the subject, apart from simple cases where it is plausible to identify sets of equally probable propositions, or where it seems reasonable to take an observed relative frequency as the initial value.

Our aim now is to develop a small part of the theory implied by the two rules we have derived; but this will be sufficient to approach the other and rather neglected aspect of the subject, which attempts to formulate rational procedures for choosing explicit numerical values for the probabilities in at least some fairly general situations. The cases we have in mind, of course, are more particularly those for which frequency data are not available and in which there are no obvious sets of primitive propositions to be taken as equally probable. The method we present, however, can also be used to justify and extend earlier ideas.

3.3 Some useful theorems

The results derived in the last subsection give rise to an extensive mathematical theory of probability. In this subsection we collect together only the few theorems that we shall need subsequently. Most of them are straightforward deductions from the basic rules, but are so useful that they should be regarded as working rules in their own right. Summarising the content of our consistent theory of probable inference, we have shown that the degree of belief in a proposition $A$, given evidence $K$, may be represented by a number $p(A|K)$, satisfying the restrictions

$$0 \leq p(A|K) \leq 1,$$  \hspace{1cm} (74)

in which the upper and lower limits denote certainty and impossibility, respectively, and that the necessary computational rules for combining such probability numbers can be reduced to the elementary forms:

Rule 1 \hspace{1cm} p(A.B|K) = p(A|B.K)p(B|K)  \hspace{1cm} (75)

and

Rule 2 \hspace{1cm} p(A|K) + p(\sim A|K) = 1  \hspace{1cm} (76)

Our first deduction follows at once from Rule(1) by using the logical relation $A.B = B.A$, so that

$$p(A.B|K) = p(B.A|K).$$  \hspace{1cm} (77)
Interchanging propositions $A$ and $B$ in Eq.(75) gives

$$p(B.A|K) = p(B|A.K)p(A|K),$$

(78)

and on combining these equations with Rule(1) we find

Rule 3

$$p(A|B.K)p(B|K) = p(B|A.K)p(A|K)$$

(79)

This simple result is known as Bayes’ Theorem and it is one of the most useful in probability theory since it codifies the process of learning from experience. To see this, suppose we are considering the probability of proposition $A$ on evidence $K$, and then acquire some new evidence $B$. Rewriting Eq.(79) in the form

$$p(A|B.K) = \left[ \frac{p(B|A.K)}{p(B|K)} \right] p(A|K)$$

(80)

we see that the prior probability $p(A|K)$, appropriate when we know only $K$, gets transformed into the posterior probability $p(A|B.K)$ as a result of the new evidence $B$. The transforming factor is the ratio of the probability of the truth of $B$, supposing that both $A$ and $K$ are given, to the probability that $B$ is implied by $K$ alone. This ratio is sometimes called the likelihood and may be either greater than or less than unity. Hence the new evidence will strengthen or weaken our belief in the truth of $A$ in a calculable way.

The next result is a generalisation of Rule(2). Writing Rule(1) first as it is, and then with $A$ replaced by $(\sim A)$, we obtain the equivalent pair

$$p(A.B|K) = p(A|B.K)p(B|K),$$

(81)

and

$$p((\sim A).B|K) = p(\sim A|B.K)p(B|K),$$

(82)

Addition of these two equations yields

$$p(A.B|K) + p((\sim A).B|K) = [p(A|B.K) + p(\sim A|B.K)]p(B|K)$$

$$= p(B|K), \text{ on using Rule(2),}$$

(83)
Thus

\[ p(A.B|K) + p(\sim A).B|K) = p(B|K). \] (84)\n
It is easily seen that Rule(2) is a special case of this last equation, arising when \( B \) is a proposition certain on evidence \( K \).

As a final general theorem we deduce a formula for the probability of the compound statement \((A \lor B)\), called the disjunction of two propositions, which asserts that either \( A \) is true or \( B \) is true or both are true. We recall that the operation of disjunction is related to the conjunction (AND) operation by

\[ \sim (A \lor B) = (\sim A).(\sim B). \] (85)\n
We now drop \( K \) temporarily and write Rule(4) in two slightly different but equivalent forms as follows

\[ p((\sim A).B) + p((\sim A).(\sim B)) = p(\sim A), \] (86)\n
\[ p(A.B) + p((\sim A).B) = p(B). \] (87)\n
The next step is to apply Rule(2) with \( A \) replaced by \((A \lor B)\):

\[ p(A \lor B) = 1 - p(\sim (A \lor B)) \quad \text{from Rule(2)} \]
\[ = 1 - p((\sim A).(\sim B)) \quad \text{from Eq.(85)} \]
\[ = 1 - p(\sim A) + p((\sim A).B) \quad \text{from Eq.(86)} \]
\[ = p(A) + p((\sim A).B) \quad \text{from Rule(2)} \]
\[ = p(A) + p(B) - p(A.B) \quad \text{from Eq.(87).} \] (88)\n
On restoring \( K \) we obtain the pleasingly symmetric theorem

\[ p((A \lor B)|K) + p(A.B|K) = p(A|K) + p(B|K). \] (89)\n
From this point on we specialise to propositions of the type exemplified in statistical mechanics.

Consider first a whole set of inferences such that our background knowledge \( K \) implies the truth of at \textit{least} one of the possibilities. This kind of set is said to be \textit{exhaustive} on \( K \). In the notation
of symbolic logic, a set of propositions \{A_m\}, \(m = 1 \to M\), which is exhaustive on \(K\), can be characterised by saying that the compound statement

\[ C = (A_1 \vee A_2 \vee \ldots \vee A_M) \]  

(90)

is certain given \(K\). But we know that the probability of a certain proposition is assigned the value unity, i.e.,

Rule 6 \[ p(A_1 \vee A_2 \vee \ldots \vee A_M) = 1. \]  

(91)

On the other hand, if the evidence \(K\) implies only that at most one of the set of propositions \{A_m\}, \(m = 1 \to M\), can be true, then every conjunction \((A_m \land A_n), m \neq n\), must be impossible given \(K\). Such a set is said to be exclusive on \(K\) and the condition is symbolised by

\[ p(A_m \land A_n | K) = 0, \quad m \neq n. \]  

(92)

Hence we have, by Rule(5), that in this case

\[ p(A_1 \vee A_2 \vee \ldots \vee A_m | K) = p(A_1 \vee (A_2 \vee A_3 \vee \ldots \vee A_M) | K) \]

\[ = p(A_1 | K) + p(A_2 \vee A_3 \vee \ldots \vee A_M | K) - p(A_1 . (A_2 \vee A_3 \vee \ldots \vee A_M) | K), \]  

(93)

The last term on the right hand side is zero by the condition of exclusion, since if \((A_1 . A_m), m > 1\) is impossible, then so is the proposition \(A_1 . (A_2 \vee A_3 \vee \ldots \vee A_M)\). Repetition of this process by separating off \(A_2\), then \(A_3\), etc., soon shows that for a set of mutually exclusive propositions

Rule 7 \[ p(A_1 \vee A_2 \vee \ldots \vee A_M | K) = \sum_m p(A_m | K) \]  

(94)

Finally, if the set of inferences \{A_m\} is both exhaustive (at least one is true) and exclusive (at most one is true) on evidence \(K\), then it is clear that exactly one of them is true, though in general we do not know which. Thus from Rules (6) and (7) we derive the special theorem, valid for a set of \(M\) exhaustive and exclusive propositions,

Rule 8 \[ \sum_m p(A_m | K) = 1 \]  

(95)

This is the appropriate place to discuss the Principle of Indifference once again, though now in a more abstract form than before. If the conditions of Rule(8) are satisfied, but the evidence \(K\)
provides no grounds for believing in any one of the propositions more strongly than in any other, then there is clearly an element of symmetry present. We know from Rule(8) that the probabilities must add up to unity, but that is all we know. A rational way to proceed is to appeal to the now familiar idea of consistency.

Suppose that some non-uniform distribution of the probabilities over the labels \( m \) is suggested, i.e., in general \( p(A_m|K) \neq p(A_n|K) \) for \( m \neq n \). But then, by permuting the propositions and relabelling them, say with the new subscript \( j = 1 \to M \), we can set up a differently ordered but equivalent collection \( \{A_j\} \) with each \( A_j \) equal to an \( A_m \) of the previous labelling. If all inferences carry with them the originally suggested probabilities, then in the new scheme the distribution over the ordering labelled by \( j \) will look quite different to the earlier distribution over the ordering specified by \( m \). Yet the new arrangement is entirely equivalent to the first with respect to the given evidence and should for consistency appear to have the same distribution over labels. The only choice of probabilities consistent with permutation invariance is to take them all equal, so for the given conditions we should have

\[
\text{Rule 9} \quad p(A_m|K) = p(A_n|K), \quad \forall m, n
\]

Combining Rule(8) and Rule(9) we obtain, at last, some definite numerical values for the probabilities of propositions which are neither certain nor impossible on the given information, but only in a very special situation. The simple result is

\[
\text{Rule 10} \quad p(A_m|K) = \frac{1}{M}, \quad \forall m
\]

for a set of \( M \) inferences \( \{A_m\} \) known only to be exhaustive and mutually exclusive on given premisses \( K \).

To conclude this subsection we discuss briefly the expected value of a function \( X \) taking on numerical values \( X_m \) for the inferences of an exhaustive and exclusive set \( \{A_m\} \). It may be necessary, as in statistical mechanics, to estimate a single value for \( X \), for comparison with, or prediction of, experimental quantities. One possibility is just to take the value of \( X \) associated with the most probable inference. This number is called the mode. However, there may not be a single
most probable inference or perhaps there are several inferences with very similar probabilities to which we would like to give some weight. There are no hard and fast rules available here, so we must rely on common sense. In many situations, especially when the appreciable probabilities are for a subset of inferences attached to similar values of $X_m$, a very reasonable guess for the expected value is the **mean**, defined by

$$\bar{X} = \langle X \rangle = \sum_m p(A_m|K)X_m,$$  

(98)

As a test of whether $\bar{X}$ is a reliable estimate it is also reasonable to consider the mean of the squared deviations of $X_m$, denoted by

$$(\Delta X)^2 = \sum_m p(A_m|K)(X_m - \bar{X})^2,$$  

(99)

and to demand that the **root mean square deviation** $\Delta X$ is, in some sense, small. It is an easy exercise to show from the definitions, and from Rule(8), that

$$(\Delta X)^2 = \langle X^2 \rangle - \langle X \rangle^2.$$  

(100)

It is also easy to show that the mean square deviation of $X$ away from any estimate $\tilde{X}$ of the expected value of $X$ is a minimum for $\tilde{X} = \bar{X}$. In the development of the formalism of statistical mechanics we shall mainly be concerned with the calculation of mean values of observable quantities, but it is frequently necessary to check that our average values are in fact **useful** predictions of the expected results of experiment. For this purpose, it is usually sufficient to calculate also the root mean square deviation from the average and verify that it is small compared to any likely measurement error. If it should, nevertheless, turn out that the observed discrepancy of the calculated mean from experiment is greater than the estimated experimental errors, then the most likely conclusion is that the model used for calculation is deficient.

### 3.4 Theory of uncertainty

For nearly three centuries the only known method for assigning initial probabilities in a calculation, apart from their approximate assessment by finite statistical experiments, was to appeal to the
Principle of Indifference or Equiprobability. As we have seen, this requires the identification of a set of exhaustive and exclusive propositions which are symmetrical with respect to the available background knowledge.

In this subsection we investigate what can be done when it is clear from the evidence $K$ that the propositions of an exhaustive and exclusive set are not all equally probable. It may happen, for example, that direct observations of a quantity associated with the possible inferences yield values systematically different from the average calculated on the basis of equal probabilities. Or one may have a strong theoretical reason for believing in the existence of a sharp mean value, as in the case of the energy of an isolated body, and want to choose probabilities consistent with such an imposed average. Almost always, however, the amount of information at our disposal is not enough to define a unique set of probabilities, and we have to select, among the many distributions which satisfy the known constraints, that which is, in some sense, the best or the most honest one. Our only guide is the strong feeling that a truly impartial choice of distribution should somehow imply the greatest possible uncertainty, about the actual situation, as is compatible with our special knowledge.

Let us therefore proceed by trying to formulate a measure of the state of doubt, or uncertainty, implied by a given probability distribution $p(A_m|K)$, $m = 1 \rightarrow M$, over a set of exhaustive and exclusive propositions $\{A_m\}$. For such probabilities we condense the notation by writing

$$p_m = p(A_m|K) \quad (101)$$

with

$$\sum_m p_m = \sum_m p(A_m|K) = 1, \quad (102)$$

by Rule(8) of the previous subsection.

On being given numerical values for different special sets of probabilities $\{p_m\}$, it is often easy to see at a glance that they represent quite markedly different states of knowledge. For instance, one set may attribute similar probabilities to many possibilities, so that a choice between them is difficult. Another may indicate several conceivable inferences, but with only one or two of them
at all likely. The first case gives a greater impression of uncertainty than the second and it is only a short step to the idea that this kind of judgement can be quantified. However, there is no guarantee that a unique measure of uncertainty can be found or even that a single number will adequately summarise our feelings of doubt.

We nevertheless postulate the existence of some numerical function of the probabilities \( \{p_m\} \), to be denoted by

\[
U_m(p_1, \ldots, p_m, \ldots p_M) = U_M(\{p_m\}),
\]

which represents by its values the overall amount of uncertainty to be associated with a given probability distribution. It is a surprising theorem that this uncertainty function is determined up to an arbitrary multiplicative constant by requiring it to satisfy two innocuous seeming but natural conditions and a simple composition rule arrived at by plausible considerations of consistency. These conditions are meant as a precise formulation of our intuitive ideas about how a measure of “Amount of Uncertainty” should behave. In particular, the notion of amount or quantity of something suggests that uncertainties should be combined by some form of addition rule. The three conditions are:

- (i) The quantity \( U_M(\{p_m\}) \) should be a smooth continuous function of its arguments. Otherwise, small adjustments of the probabilities may lead to large changes in the uncertainty, which would seem highly unreasonable.

- (ii) If all \( p_m = 1/M \), so that the function \( U_M \) has \( M \) equal arguments and depends only on \( M \), i.e.,

\[
U_M(1/M, \ldots, 1/M) = f(M),
\]

then \( f(M) \) should be a monotonically increasing function of \( M \). Clearly, the larger the number of equally probable possibilities the greater should be our uncertainty about which one is true.

- (iii) Different ways of evaluating the numerical value of \( U_M(\{p_m\}) \) should give the same answer. This condition of consistency can be turned into a definite statement only by
specifying alternative routes for arriving at the answer.

Instead of giving the probabilities \(\{p_m\}\) for the individual propositions \(\{A_m\}\) directly, we might provide equivalent information in two stages. Suppose we group the first \(r\) propositions into a compound block

\[
B_1 = (A_1 \lor A_2 \lor \ldots \lor A_r),
\]

the next \(s\) propositions into the block statement

\[
B_2 = (A_{r+1} \lor A_{r+2} \lor \ldots \lor A_{r+s}),
\]

and so on, until we have \(N\) blocks \(\{B_i\}\), \(i = 1 \rightarrow N\), altogether and all the \(\{A_m\}\), \(m = 1 \rightarrow M\) are used up. Then, information equivalent to the \(\{p_m\}\) values is specified by giving the set of probabilities for the blocks, \(\{P_i = p(B_i|K)\}\), followed by all the conditional probabilities \(\{p(A_m|B_i.K)\}\) for an \(A_m\) to be the true proposition, given that it occurs in a block \(B_i\).

From Rule(7), and the definition of the \(\{B_i\}\), we have

\[
P_1 = \sum_{m=1}^{r} p_m, \quad P_2 = \sum_{m=r+1}^{r+s} p_m, \quad \text{etc.,}
\]

and it is clear that the \(\{P_i\}\) satisfy the condition

\[
\sum_{i=1}^{N} P_i = \sum_{m=1}^{M} p_m = 1.
\]

Thus the probabilities of the \(N\) exhaustive and exclusive block statements \(\{B_i\}\) contribute to an amount of uncertainty

\[
U_N(P_1, P_2, \ldots, P_N) = U_N(\{P_i\}).
\]

To see how the specified conditional probabilities \(\{p(A_m|B_i.K)\}\), within the blocks, are related to the original probabilities \(\{p_m\}\) consider in particular the conjunction \((A_m.B_1)\). This asserts that \(A_m\) is true and simultaneously that one of the propositions in the first block is true. Thus the probability \(\{p(A_m.B_1|K)\}\) can be non-zero only for propositions in the first block, and we have easily that

\[
p(A_m.B_1, |K) = p_m, \quad 1 \leq m \leq r
\]

\[
= 0, \quad r+1 \leq m \leq M,
\]
But by Rule\((1)\) of the previous subsection we know that

\[
p(A_m B_1 | K) = p(A_m | B_1, K) p(B_1 | K)
\]

and, since \(p(B_1 | K) = P_1\) is just the probability of block \(B_1\), the required conditional probabilities are expressed by

\[
p(A_m | B_1, K) = \frac{p_m}{P_1}, \quad 1 \leq m \leq r
\]

\[
p(A_m | B_2, K) = \frac{p_m}{P_2}, \quad r + 1 \leq m \leq r + s
\]

and similarly for all \(N\) blocks. Now, on evidence \((B_1, K)\), the \(r\) statements \(\{A_m\}, 1 \leq m \leq r\), of the first block, form an exhaustive and exclusive set with

\[
\sum_{m=1}^{r} p(A_m | B_1, K) = \sum_{m=1}^{r} \frac{p_m}{P_1} = 1,
\]

so we see that the internal uncertainties of the blocks can be represented by expressions of the type

\[
U_r\left(\frac{p_1}{P_1}, \ldots, \frac{p_r}{P_1}\right), U_s\left(\frac{p_{r+1}}{P_2}, \ldots, \frac{p_{r+s}}{P_2}\right), \text{ etc.}
\]

To compute the final answer, we note that each of these uncertainties is encountered only with the associated block probability; hence they should be weighted with those probabilities and added to the uncertainty \(U_N(\{P_i\})\) arising from the choice of blocks. An alternative computational path has now been specified and the result, for consistency, should be the same as before, i.e.,

\[
U_M(p_1, \ldots, p_M) = U_N(P_1, \ldots, P_N) + P_1 U_r\left(\frac{p_1}{P_1}, \ldots, \frac{p_r}{P_1}\right) + P_2 U_s\left(\frac{p_{r+1}}{P_2}, \ldots, \frac{p_{r+s}}{P_2}\right) + \ldots
\]

This form of composition rule is required to hold for all possible regroupings of the original propositions, and in each case the two sides of the equation will contain exactly the same probability information, though differently arranged. Our formulation of the consistency condition is now complete. However, it must be admitted that the argument leading to the above formula is not entirely compelling. It would seem more natural to equate the total uncertainty to the direct sum of external and internal block uncertainties rather than to weight the latter quantities with the corresponding block probabilities before summing. Such a scheme does not lead to a useful result.
and we must therefore conclude that the proper and convincing form of words to justify exactly the given rule has not yet been found. In spite of this, we observe that the exhibited composition formula is still a very reasonable embodiment of consistency.

It is not difficult to verify that, for any constant $\alpha > 0$, all three of our conditions are satisfied by the function

$$U_M(p_m) = -\alpha \sum_{m=1}^{M} p_m \ln (p_m),$$

and Shannon\cite{17} has shown that it is unique. This expression neatly captures the essence of uncertainty and has remarkable mathematical properties that we shall indicate and use later on. It was originally developed by Shannon in connection with work on the efficient encoding and transmission of messages, but it has turned out to have significance for many other problems involving probabilities. What it is important to observe is that the derivation makes no reference to physics, though the result can in fact be applied very effectively in that special field. Indeed, our interest in the uncertainty function arises precisely because it may be used as the basic tool for a rational choice of probability distributions in statistical mechanics.

### 3.5 Assignment of probabilities

The uncertainty is sometimes called the *missing information* of a probability distribution since it can be thought of as representing the extra knowledge required to reduce all doubts to zero, i.e. to determine the true proposition. It should be clear, however, that any distribution of probabilities conditional on evidence $K$ always embodies *some* knowledge about the situation, even if only, as in the special cases we have considered, that we are dealing with propositions which are exhaustive and mutually exclusive. When it comes to assigning probabilities, we want to be sure that the selected distribution is a true reflection of the knowledge we really have, and does not have unwarranted assumptions built into it. A reasonable proposal, therefore, is that the most honest probabilities compatible with the known data are the ones for which our uncertainty, or missing information, is still as large as possible. The definite measure established for this lack of knowledge can then be used as a predictive instrument, as follows. The least
committal probability distribution among all those that conform with the actual data, is that which maximises the missing information \( U_M(\{p_m\}) \). This solves the initial assignment problem in many interesting cases.

The above suggestion has been called by Jaynes the Principle of Maximum Entropy \[23\], since the measure of uncertainty was originally called entropy by Shannon \[17\]. Notice particularly that it is \textit{not} claimed that the probabilities thus produced are the final word or are in any sense the \textit{real} ones. There are no such things as real physical probabilities, only codings of our current state of knowledge, and the algorithm yields those codings which represent, in a well-defined impartial way, just our actually existing information, and nothing else. The power of the principle becomes apparent only when the maximum entropy probabilities are used to estimate a quantity before it is observed. It is interesting if the prediction is successful, but even more interesting if it is not, since that indicates the presence of some previously unknown constraint.

If the constant in the formula for the uncertainty is chosen to have the value \( \alpha = 1 \) the resulting function will be written as \( \sigma(\{p_m\}) \) and called the \textit{information entropy} for the probabilities of \( M \) exhaustive and exclusive propositions. Explicitly

\[
\sigma(\{p_m\}) = -\sum_m p_m \ln (p_m) \tag{117}
\]

with

\[
\sum_m p_m = 1 \quad \text{always} \tag{118}
\]

and we can state the formal rule to be known as:

- **Jaynes' Principle**: Probabilities should be chosen so as to render \( \sigma(\{p_m\}) \) an absolute maximum, subject only to the constraints imposed by the data \( K \)[18] [21] [24].

Pending further investigation we shall assume that a distribution found in this way is unique, so that the maximising set \( \{p_m(K)\} \) depends solely on the evidence \( K \). In some problems it is also convenient to allow \( M \) to approach infinity, provided that the constraints ensure convergence of \( \sigma(\{p_m\}) \).
Before applying Jaynes’ Principle, we consider a few mathematical properties of the expression for Information Entropy, the most obvious being that $\sigma > 0$ if $0 < p_m < 1$ for all $m$. One potential source of difficulty can be cleared up quickly. If some particular $A_m$ is impossible on the evidence, then $p_m = 0$, and the corresponding term in the entropy seems ill defined. But as $x \to 0$, $x \ln(x) \to 0$; so we make the convention that $-p_m \ln(p_m) = 0$ when $p_m = 0$. This is reasonable since there is no uncertainty associated with an impossible inference — we know it is not true. The convention also implies a reasonable result when one of the $A_m$ is certain, i.e. $p_m = 1$, which entails that $p_n = 0$ for $n \neq m$. The contribution of the vanishing probabilities is zero and the entropy reduces to $\sigma = -\ln(1) = 0$. Clearly there should be no uncertainty associated with a certain proposition either. Thus we have established that $\sigma(\{p_m\}) \geq 0$ for any distribution and that $\sigma$ reaches its lower limit of zero when one of the inferences is certain.

A more interesting inequality arises if we take any pair of probabilities, say $p_1$ and $p_2$, and make them more nearly equal while keeping their sum constant. It is straightforward to prove that this increases the entropy. For a constant sum $p_1 + p_2 = C$, write $p_1 = p$ and $p_2 = C - p$, and consider the varying part of $\sigma(\{p_m\})$, namely

$$f(p) = -p \ln(p) - (C - p) \ln(C - p),$$

as a function of $p$. Its derivative is $df/dp = \ln[(C - p)/p]$, and it follows easily that $df/dp = 0$ for $p = C/2$ and that $df/dp$ is greater than or less than zero, respectively, according as $p$ is less than or greater than $C/2$. Hence any change towards equality of probabilities, while retaining the condition $\sum p_m = 1$, increases $\sigma$.

This brings out a very attractive feature of the Entropy Principle. The process of maximising $\sigma$ consists of adjusting the $\{p_m\}$, without violating any constraints, to make their differences as small as possible. The effect, as mentioned earlier, is to spread out the probability as evenly as is consistent with the data, which agrees nicely with the idea of honest assessment. Naturally, in the presence of several constraints, it will not in general be possible to make all the probabilities equal to each other. When, however, the condition $\sum p_m = 1$ is the only constraint, the above result
shows immediately that the absolute maximum of \( \sigma \) is achieved by taking all the probabilities equal, for then no further adjustment can increase the entropy. Hence we must have \( p_m = 1/M \) for all \( m \), and we have recovered the Principle of Indifference as a special case of the entropy algorithm. The corresponding maximised value of the information entropy is found to be

\[
\sigma(\{1/M\}) = \ln(M).
\]  

(120)

Any additional data beyond \( \sum p_m = 1 \) may still be consistent with equal probabilities, but is more likely to imply some differences between them; so, under further constraints, the entropy maximum must in general be less than the above value. Thus extra knowledge usually reduces the uncertainty, as we would expect.

The interpretation of entropy as missing information also looks very natural in the light of the above formula. For we have \( \ln(M) \approx \log_2(M) \), which is a good estimate of how many questions, with yes/no answers, are necessary to be sure of locating the true proposition among \( M \) equally likely possibilities. If for example \( M = 32 \), then \( \log_2(32) = 5 \) questions of the type “Is it in the first sixteen?” and so on, which halve the number of possibilities at each stage, will always ensure success. For other given probability distributions the expected number of necessary questions is similarly proportional to the value of \( \sigma(\{p_m\}) \).

Several other properties of the uncertainty function will be derived in the next section; we have said enough, for the moment, to justify its use as a tool for assigning probabilities by the Maximum Entropy Principle. Alternative derivations of the method have been given in the last few years, which may be more appealing to some tastes, but they tend to be more technical than the simple argument presented here. Before leaving the topic, however, we should mention briefly one completely independent approach to the maximum entropy idea. This is to base the method firmly on the Principle of Indifference, to bypass entirely any general discussion of uncertainty, and to consider instead how one might generate a probability distribution satisfying given constraints. In other words we set out to analyse the likely behaviour of a device for producing such distributions automatically.
Imagine a row of $M$ boxes into which $N$ similar small objects are somehow placed, preliminary observations having indicated no reason for supposing that any box is favoured as a receptacle. All we know is that every object finishes up in some box. By the Principle of Indifference, each of the $M^N$ ways of distributing the objects is equally likely; but, in general, a final result consisting only of the set $\{n_m\}$, where $n_m$ is the number of objects in the $m$'th box, can be achieved in many ways, differing merely in the order of placing the objects. The numbers $\{n_m\}$ must, by hypothesis, satisfy the condition $\sum_m (n_m/N) = 1$, and by counting the number of ways of choosing $N$ things $n_m$ at a time, without regard for order, we find that the probability for generating the set $\{n_m\}$ is

$$P(\{n_m\}) = \left[ \frac{N!}{\prod_m n_m!} \right] M^{-N}. \quad (121)$$

Now the ratios $(n_m/N)$ will serve as probability values $p_m$ and they can be made as fine as we like by taking $N$ indefinitely large. The above expression then becomes the probability of a mechanically generated probability distribution $\{p_m = (n_m/N)\}$ satisfying $\sum_m p_m = 1$. Hence on using Stirling’s Theorem in the simplified form

$$x! \approx x^x \quad (122)$$

which is valid for indefinitely large factorials, we soon find that

$$P(\{p_m\}) \approx \left[ \frac{\exp \left[ \sigma(\{p_m\}) \right]}{M} \right]^N, \quad (123)$$

where

$$\sigma(\{p_m\}) = -\sum_m p_m \ln (p_m) \quad (124)$$

is the by now familiar entropy function, which we already know satisfies $\sigma \leq \ln (M)$. If we choose to consider only the distributions $\{p_m\}$ which satisfy some specified constraints, then clearly the most probable distribution generated in this way is the one which maximises $\sigma$ subject to the constraints.

Furthermore, the ratio of probabilities for the maximising distribution $\{p_m\}_{\text{max}}$ and any other set $\{\tilde{p}_m\}$ consistent with the same data, is given by

$$\frac{P_{\text{max}}}{P} = \exp \left[ N(\sigma_{\text{max}} - \tilde{\sigma}) \right], \quad (125)$$

53
which increases rapidly with $N$. So, for large $N$, the maximum entropy distribution is overwhelmingly the most likely to be generated. We may therefore conclude that, in a very definite sense, the methods we have explained yield the most probable probability distribution conforming to our knowledge of the situation.
4 Uncertainty and entropy

4.1 Isolated equilibria

The material of the second section was intended as a simple preliminary discussion of the main problem to be solved before the properties of a body at equilibrium can be estimated. A system with observables constant in time is reasonably described in terms of energy eigenstates and we require to know which eigenstate occurs. Since it is unreasonable to suppose that the exact eigenstate occurring can be determined, the best we can hope to do is to assign probabilities to the possible states and to estimate the measurable quantities by averaging. The ensuing account of probability theory in the third section was purposely kept rather abstract in order to emphasise that the methods used for assigning the probabilities do not, in themselves, depend in any way on the mechanics of bodies; the physics of the situation enters only when the general method is applied to find the eigenstate probabilities consistent with our background knowledge.

The earlier discussion was based on the assumption that an isolated body, with known Hamiltonian $\hat{H}$, was in some normalised state $|\Psi(t)\rangle$, which developed in time according to the Schrödinger equation

$$\hat{H}|\Psi_\alpha(t)\rangle = i\hbar \frac{\partial |\Psi_\alpha(t)\rangle}{\partial t}, \quad (126)$$

where we have now attached to $|\Psi\rangle$ a subscript $\alpha$ to denote all the labels required to specify the state.

As soon as we realise that the available data $K$ are never sufficient to determine $|\Psi_\alpha\rangle$ uniquely, it is clear that the previous treatment has to be generalised. To do this we suppose that $|\Psi_\alpha(t)\rangle$ is one member of a complete set of states $\{|\Psi_\alpha(t)\rangle, |\Psi_\beta(t)\rangle, \ldots\}$, orthonormal at $t = 0$. Thus, for any $\alpha$ and $\beta$,

$$\langle \Psi_\alpha(0)|\Psi_\beta(0)\rangle = \delta_{\alpha\beta}. \quad (127)$$

It then follows easily from the wave equation that this orthonormalisation is preserved at all later times $t > 0$. Hence the states $\{|\Psi_\alpha(t)\rangle, \ldots\}$ form an exhaustive and exclusive set of possibilities for description of the system and, with any evidence $K$, each will occur with some probability.
\( p(\alpha|K) \), where \( \sum_\alpha p(\alpha|K) = 1 \).

The discussion of what happens, on the hypothesis that the state is \( |\Psi_\alpha(t)\rangle \), is essentially the same as before. If we wait long enough, the time dependence of reproducible macroscopic properties will effectively damp out and our estimates of energy and other quantities in state \( |\Psi_\alpha\rangle \) take on the constant equilibrium forms

\[
\langle E \rangle_\alpha = \sum_j \langle \psi_j | \hat{H} | \psi_j \rangle p(j|\alpha)
\]

and

\[
\langle Q \rangle_\alpha = \sum_j \langle \psi_j | \hat{Q} | \psi_j \rangle p(j|\alpha)
\]

In these expressions the matrix elements are expectation values with respect to energy eigenstates \( |\psi_j\rangle \), defined by \( \hat{H}|\psi_j\rangle = E_j|\psi_j\rangle \); and, from the rules of quantum mechanics, the probabilities associated with the energy eigenstates are given by \( p(j|\alpha) = |a_j^\alpha|^2 \), where the amplitudes \( a_j^\alpha \) are the constant coefficients of the expansion of the system state in energy eigenfunctions, i.e.,

\[
|\Psi_\alpha(t)\rangle = \sum_j a_j^\alpha |\psi_j\rangle \exp\left(-E_j t/\hbar\right).
\]

The probabilities \( \{p(j|\alpha)\} \) are thus evaluated on the explicit assumption that the actual state is \( |\Psi_\alpha(t)\rangle \). However, in order to obtain useful estimates of the system observables we must also take specific note of the probabilities \( \{p(\alpha|K)\} \) for the occurrence of the states of the set \( \{|\Psi_\alpha(t)\rangle\} \). A very reasonable plan is to construct the mean values

\[
\hat{E} = \sum_\alpha \langle E \rangle_\alpha p(\alpha|K)
\]

and

\[
\hat{Q} = \sum_\alpha \langle Q \rangle_\alpha p(\alpha|K),
\]

from which, on remembering that \( \langle \psi_j | \hat{H} | \psi_j \rangle = E_j \), we find the mean energy

\[
\bar{E} = \sum_{\alpha,j} E_j p(j|\alpha) p(\alpha|K),
\]

while for the mean values of other quantities we finish up with

\[
\bar{Q} = \sum_{\alpha,j} \langle \psi_j | \hat{Q} | \psi_j \rangle p(j|\alpha) p(\alpha|K).
\]
Now, by Bayes’ Theorem, Rule(3) of subsection 3.3, we have that

\[ p(j|\alpha)p(\alpha|K) = p(j,\alpha|K) = p(\alpha|j,K)p(j|K), \]  

which leads immediately to the conclusion that

\[ \sum_{\alpha} p(j|\alpha)p(\alpha|K) = p(j|K)\sum_{\alpha} p(\alpha|j,K). \]  

Moreover, we have by hypothesis that the states \( \{\Psi_\alpha(t),\ldots\} \) form an exhaustive and exclusive set of possibilities, on any evidence. Hence \( \sum_{\alpha} p(\alpha|j,K) = 1 \) and we see that the mean values reduce to

\[ \bar{E} = \sum_{j} E_j p(j|K) \]  

and

\[ \bar{Q} = \sum_{j} \langle \psi_j | \hat{Q} | \psi_j \rangle p(j|K). \]  

The upshot of this more careful discussion is, that when equilibrium is reached, it is not necessary to consider what the actual state of the system might be, but only to assign probabilities for the various energy eigenstates on the basis of the data \( K \). Clearly, the energy states \( \{|\psi_j\rangle\ldots\} \) are also exhaustive and exclusive on any evidence \( K \), since a measurement of energy must always result in some particular eigenstate. Thus the finally required probabilities \( \{p(j|K)\} \) must satisfy the condition \( \sum_{j} p(j|K) = 1 \).

We are now faced with exactly the type of problem envisaged in Jaynes’ Principle\[18, 21, 24\]. There are \( M \) possibilities, where \( M \) may be indefinitely large, or even denumerably infinite, to be considered in the light of given data \( K \). The most impartial assignment of the respective probabilities is achieved by maximising the information entropy

\[ \sigma(\{p_j\}) = -\sum_{j} p_j \ln(p_j), \]  

subject to probability normalisation and the constraints implied by \( K \). Assuming that there is a unique maximising distribution, which needs to be checked in each case, the resulting probabilities \( p(j|K) \) will depend on the data \( K \) and may be used to construct the mean values of observables
for comparison with experiment. The actual implementation of this programme, for the most
commonly considered types of assumed prior knowledge, will be spelt out in the next section.
Notice, however, that once the probabilities have been decided on there appears to be no further
use for the uncertainty function \( \sigma \). While this is, strictly speaking, correct, since everything of
experimental interest can be calculated from the probabilities, it is not entirely idle to investigate
the physical meaning of the maximised uncertainty.

The most important remark is that the existence of a unique maximising distribution \( \{p(j|K)\} \)
implies that the corresponding maximal value of the information entropy

\[
\sigma_{\text{max}}(\{p(j|K)\}) = \sigma_{\text{max}}(K)
\]

(140)
is a function of the assumed data. We shall show that the function \( \sigma_{\text{max}}(K) \) possesses all the
properties of the thermodynamic entropy \( S \). In fact we shall try to make plausible the definite
identification

\[
S = k_B \sigma_{\text{max}}(K) + S_c,
\]

(141)
in which \( k_B \) is a constant determined by the experimental definition of \( S \), and \( S_c \) is an arbitrary
constant. Such a demonstration amounts to a detailed statistical interpretation of the thermody-
namical entropy.

The theoretical formula for entropy as maximal uncertainty has a definite mathematical ex-
pression for each specific “system plus relevant data”. It depends both on the structure of the
body and on what we have chosen to measure, and this is also true of the experimental entropy \( S \).
It is clearly very useful to be able to identify \( \sigma_{\text{max}}(K) \) with \( S(K) \), in suitable units, for then all the
well-developed machinery of thermodynamics can be applied to the statistical expression. This
enables rapid derivations of results in statistical mechanics which would be tedious to construct
directly.

4.2 Thermodynamic entropy

We proceed by examining some of the well-known properties of thermodynamic entropy \( S(K) \), with
the ultimate aim of showing mathematically that \( \sigma_{\text{max}}(K) \) has the same properties. To connect the
mathematics with the physics we shall assume throughout that statistically calculated mean values \( \bar{Q} \) are accurate estimates of the corresponding observed quantities; it will then become highly plausible that \( S \) and \( \sigma_{\text{max}} \) should be closely related. We note first that in classical thermodynamics nothing is assumed about the microscopic structure of bodies, but that a large accumulation of experience may be understood by postulating the existence of an entropy function \( S \) with the following properties:

- (i) It is defined for equilibrium conditions,
- (ii) is a function of the “state” of the system,
- (iii) is not decreased by an adiabatic process,
- (iv) is an extensive or additive variable, and
- (v) is related experimentally to heat and temperature.

Each of these items is also characteristic of our maximised uncertainty function. The first two are included for the sake of completeness and can be disposed of relatively quickly. To show that \( \sigma_{\text{max}} \) possesses the next two properties is more complicated, but the proofs depend only on general considerations. The last item alludes to the definite experimental procedure for measuring entropy which underlies the formulation of the previously listed properties. We shall defer the demonstration, that maximised uncertainty is determined empirically by exactly the same procedure, until the appropriate probability distribution has been derived. In this section we concentrate attention on the first four listed properties of \( S \) and \( \sigma_{\text{max}} \).

**Equilibrium Restrictions:** The entropy \( S \) is traditionally introduced as a quantity which has meaning only for the macroscopically static condition of equilibrium. Its application to processes arises from the possibility of comparing values of \( S \) in initial and final equilibrium states. Such comparisons may be used, for example, to indicate what final state a system will reach after internal constraints have been removed; but nothing is predicted about rates of evolution or relaxation times. The experimental entropy is not usually even defined for the intermediate time-varying
states of a process unless the changes are so gradual that the body is in effective equilibrium at all stages. Processes fulfilling the last condition are said to be quasi-static and are considered precisely for the purpose of measuring or computing entropy differences.

The uncertainty $\sigma$ is also introduced primarily as a means of describing equilibrium conditions, though in a more microscopic and theoretical way than $S$. The probabilities for the possible energy eigenstates are found by maximising $\sigma(\{p_j\})$ subject to appropriate macroscopically static constraints. Hence $\sigma_{\text{max}}(K)$ can be defined for equilibrium data $K$ and, by obvious extension, for the intermediate states of a quasi-static process. We shall soon show that knowledge of the function $\sigma_{\text{max}}(K)$ provides the same sort of information about processes as that given by $S(K)$. More generally, and by using data on rates of change, it is possible to formulate an uncertainty function which applies even in non-static intermediate situations. This at least suggests that the concept of entropy need not be restricted solely to equilibrium conditions, but discussion of such a far-reaching generalisation of ordinary thermodynamics and statistical mechanics will not be attempted here.

**State Functions:** That the entropy $S$ and uncertainty $\sigma$ are both functions of the equilibrium data $K$ is expressed conventionally by saying that they are state-functions. But the word “state” has also been used to denote the quantum wave-vector of the system. The two meanings of the word are quite distinct and it should always be clear from the context whether we are referring to the quantum state of the body or to the available data at equilibrium. It is perhaps worth remarking that, whatever the actual physical conditions in the body, the thermodynamic state is defined entirely and solely in terms of the measured data.

The statistical quantity $\sigma_{\text{max}}(K)$ is a state-function by construction, but the discovery of that special function of equilibrium data which is denoted by $S(K)$ was the central result of classical thermodynamics. The point is that thermal processes are described experimentally in terms of the non-integrable differential $dq$ of heat transfer, so it was certainly of fundamental interest that there exists a universal integrating factor which converts $dq$ into the perfect differential $dS$. A more extensive discussion of this will be given in the next section when we describe exactly how $S$
or $\sigma_{\text{max}}$ may be measured. For the moment we shall just indicate in a general way how $S$ depends on the state.

The required equilibrium data must include an estimate of the mean energy $\bar{E}$ of the system and the values of selected external and internal parameters, typically the volume $V$ and the number of atoms $N$. These are meant only as examples and it is quite possible that other controllable parameters will eventually have to be specified in order to understand the full range of behaviour of the system. With this proviso, the entropy may be written as a function of experimental data in the form

$$S = S_{\text{exp}}(K, K_0) + S_0,$$

where $K \equiv (\bar{E}, V, N)$ and $K_0 \equiv (\bar{E}_0, V_0, N_0)$ are corresponding data for an equilibrium reference state with arbitrarily assigned entropy $S_0$. The entropy $S_{\text{exp}}(K, K_0)$ is determined empirically from the results of certain specific measurements of temperature and heat transfer, as the system is caused to undergo a quasi-static change from the arbitrary reference state $K_0$ to the final condition with data $K$. When the function has been mapped out over a sufficient domain of data, physical predictions about the system follow by differentiation or by comparing values of $S$ in the different states of equilibrium. In all such applications of the concept of entropy the final results are independent of the arbitrary constant $S_0$ and the initial reference state $K_0$.

The microscopic description of equilibrium in terms of energy eigenstates also makes essential use of the data $K$. In particular, the energy operator $\hat{H}$, which determines the eigenstates $\{|\psi_j\rangle\}$, depends on various parameters such as $V$ and $N$, and the corresponding energy eigenvalues are the functions $E_j(V,N)$. It is usually assumed in addition that the system possesses a definite mean energy $\bar{E}$. Hence a normalised probability distribution for the eigenstates must satisfy, at least, the constraints

$$\sum_j p_j = 1 \quad \text{and} \quad \sum_j E_j(V,N)p_j = \bar{E}.\quad (143)$$

The unique maximal uncertainty consistent with these restrictions will thus depend on the same data, $K \equiv (\bar{E}, V, N)$, as is required for definition of $S$, i.e., we have $\sigma_{\text{max}} = \sigma_{\text{max}}(K)$. 

No mention is made here of a reference state $K_0$, or of any arbitrary additive constant, because the maximised uncertainty is an absolute quantity and has a natural zero in which the exact eigenstate of the body is known. The reason for this difference is that $\sigma_{\text{max}}(K)$ has so far been formulated as a theoretical expression whose explicit construction depends on a detailed knowledge of the eigenvalue spectrum of the system Hamiltonian as well as on the given data. Technically, it is a function of $K$ and a functional of the eigenspectrum. To prove the basic identity of the functions $\sigma_{\text{max}}$ and $S$ we will certainly need to show that the quantum information can be replaced to some extent by a knowledge of just those thermodynamic measurements which are needed to evaluate $S$. It will then become plain that experimental determinations of $\sigma_{\text{max}}(K)$ are necessarily relative to an initial equilibrium reference state $K_0$ and that they leave undetermined an arbitrary constant representing $\sigma_{\text{max}}(K_0)$.

On the other hand it is sometimes feasible to obtain direct experimental information on the energy spectrum, from which the function $\sigma_{\text{max}}(K)$ may be calculated as an absolute quantity. Comparison of its variation with $K$ to that of the function $S(K)$ then gives objective support to the idea that the two concepts are intimately related. Several interesting insights into thermal behaviour have been obtained as by-products. For instance, the theoretical formula leads at once to a statistical interpretation of the Nernst Postulate on entropy, sometimes called the Third Law of Thermodynamics. Before discussing such relatively minor matters, however, we shall show in the next subsection how to prove the probabilistic analogue, for $\sigma_{\text{max}}(K)$, of the Second Law of Thermodynamics governing the behaviour of $S(K)$.

4.3 Adiabatic processes

When the properties of an otherwise isolated body are changed by altering the configuration of the confining walls, or by modifying the applied fields, or by adjusting the mechanical stresses acting on it, in a controllable way, the process is said to be adiabatic. The effect is that the system Hamiltonian is varied in a definite knowable manner and, in general, work is done on the system. Bodies may also be subjected to processes in which no obvious mechanical work is done on them,
as when they are exposed to a flame, or are placed in an oven or a refrigerator. Such non-adiabatic processes always involve the presence of another body which can exchange energy with the given system in a mechanically uncontrollable way. In essence, the effective Hamiltonian of the given body suffers unpredictable or random perturbations which are not macroscopically recognisable as work. This kind of energy transfer is called heating (or cooling), and for a pure heating process the Hamiltonian of the body at the end is the same as at the start of the operation. For an adiabatic process the system Hamiltonian at the end may be the same or may be different from the initial one, but in either case the energy gained or lost by the body can be calculated from external mechanical measurements. In a heating process this is not possible and the final energy transfer can only be determined by direct measurement of the difference between the initial and final energies of the body. The most general type of process involves both heating and working.

The heating of a body takes place by radiation, conduction or convection of energy to or from the outside world. In practice, it is often possible to surround the system with heat-proof walls which, to a good approximation, isolate it from these microscopically random influences. The fundamental law of entropy change to be discussed now applies only under such conditions of adiabatic isolation. This rule is one version of the Second Law of Thermodynamics and it states that the entropy of a body never decreases as the result of a reproducible adiabatic process. It is assumed there that the system starts and finishes in a condition of complete thermodynamic equilibrium, with the initial and final entropies $S(\bar{E}_I, V_I)$ and $S(\bar{E}_F, V_F)$ determined entirely by the corresponding equilibrium data. We have suppressed the dependence of $S$ on the number $N$ of atoms in the body, on the understanding that $N$ is constant for an isolated system. The mathematical expression of this version of the Second Law is that, for any adiabatic transformation,

$$S(\bar{E}_F, V_F) \geq S(\bar{E}_I, V_I). \quad (144)$$

It follows immediately from this relation that any equilibrium condition with entropy less than that of the initial state of the body is adiabatically inaccessible. The existence of equilibria which can not be reached from a given initial condition by the performance of work alone is a primitive
experimental observation. Indeed, Carathéodory\textsuperscript{[26]} was able to base thermodynamics precisely on the general principle that, in the neighbourhood of any equilibrium state, there are adiabatically unattainable states. From this he deduced mathematically the existence of an entropy function $S$ obeying the above inequality. However, we do not propose to discuss here the various axiomatic foundations of thermodynamics; we shall just take it as well-confirmed that there is a function $S$, depending on experimental data, which satisfies the law we have stated. Our concern is to show that the maximised uncertainty function $\sigma_{\text{max}}(\bar{E},V)$ has the same property.

Consider, therefore, an isolated body which is in equilibrium at initial time $t = 0$. If the initial Hamiltonian is $\hat{H}_I$ and the data are $K_I = (\bar{E}_I,V_I)$, then by maximising the uncertainty function, subject to $K_I$, we derive the probabilities \{$p_j(I)|K_I = p_j(I)\}$ for the occurrence of the orthonormalised energy eigenstates \{|$\psi^I_j \rangle$ = |$\Psi^I_j(t = 0)$\\} which satisfy

$$\hat{H}_I|\Psi^I_j(0)\rangle = E^I_j|\Psi^I_j(0)\rangle.$$ \hspace{1cm} (145)

The corresponding initial information entropy is represented by

$$\sigma_{\text{max}}(\bar{E}_I,V_I) = - \sum_j p_j(I) \ln (p_j(I)).$$ \hspace{1cm} (146)

Now suppose the system is caused to undergo an adiabatic change involving controlled work done on it, or by it. This is described theoretically by means of the time-dependent Hamiltonian

$$\hat{H}(t) = \hat{H}_I + \hat{W}(t).$$ \hspace{1cm} (147)

where $\hat{W}(t)$ is the potential energy operator of the forces acting on the body. Eventually the work process will cease, say at $t = t_c$, so that the final potential energy operator, $\hat{W}_F = \hat{W}(t_c)$, is constant for all $t \geq t_c$. The final Hamiltonian of the body is thus given by

$$\hat{H}_F = \hat{H}_I + \hat{W}_F, \quad t \geq t_c.$$ \hspace{1cm} (148)

The system is then allowed to come to equilibrium once more, with the Hamiltonian $\hat{H}_F$ and freshly measured equilibrium data $K_F = (\bar{E}_F,V_F)$. This final equilibrium condition will naturally be described, via the maximisation of uncertainty, by the new probabilities \{$q_m(F)|K_F = q_m(F)$\},
which refer to the occurrence of energy eigenstates \(|\varphi^F_m\rangle\) defined by
\[
\hat{H}_F|\varphi^F_m\rangle = E^F_m|\varphi^F_m\rangle.
\]

The appropriate final information entropy at the end of the adiabatic process, when equilibrium has again been reached, takes the form
\[
\sigma_{\text{max}}(\tilde{E}_F, V_F) = -\sum_m q_m(F) \ln (q_m(F)),
\]

and we require to show that, necessarily,
\[
\sigma_{\text{max}}(\tilde{E}_F, V_F) \geq \sigma_{\text{max}}(\tilde{E}_I, V_I),
\]
i.e. that the uncertainty can never decrease in this type of change. The demonstration has some subtle points, so we shall develop it slowly. It proceeds in two main stages, with the hardest, but essential, step being the proof of an intermediate inequality. We shall also need to discuss carefully an often repeated objection to the derivation, which we shall show is based on a common misinterpretation of the formalism.

We observe first that the varying Hamiltonian \(\hat{H}(t)\) is supposed known. Accordingly, it is possible in principle to follow the evolution of the system by integrating the wave equation
\[
\hat{H}(t)|\Psi(t)\rangle = i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t},
\]
from \(t = 0\) to \(t > t_c\), with the initial condition that \(|\Psi(0)\rangle\) is one or other of the eigenstates \(|\Psi^I_j(0)\rangle\), of \(\hat{H}_I\), that we started with. Thus by the time \(t = t_F > t_c\), that the system has come to equilibrium again, the functions \(|\Psi^I_j(t)\rangle\) will have evolved into the predictable states \(|\Psi^I_j(t_F)\rangle\), which remain orthonormal, but are in general no longer eigenstates of either \(\hat{H}_I\) or \(\hat{H}_F\). Furthermore, each of them will occur with the initial probability \(p(j(I)|K_I) = p_j(I)\) since no information is lost by integrating the Schrödinger equation. This is true because the equation is of first order in time, implying that the final state is determined uniquely by \(\hat{H}(t)\) and the initial state. Hence, for any such reproducible process, we should be able to predict the values of the observables at the final equilibrium by using estimates of the form
\[
\tilde{Q}_F = \sum_j \langle \Psi^I_j(t_F)|\hat{Q}|\Psi^I_j(t_F)\rangle p(j(I)|K_I),
\]
which we assume would agree with direct experimental measurements on the system. This last assumption is actually the crux of the matter, as we shall see; but is really saying no more than that we believe in the correctness of quantum theory.

From the given postulate it follows that a knowledge of the initial set of probabilities, and of the time-developed wave functions originating from the eigenstates of $\hat{H}_I$, is sufficient to deduce the properties of the final situation. In a sense, therefore, the information entropy at the end of the process, as calculated from the constant probabilities, is exactly the same as the maximised uncertainty $\sigma_{\text{max}}(I)$ of the initial set-up. In other words, our initial uncertainty about the actual state of the system will not be increased if the final state-vectors are uniquely and controllably determined from the initial ones as is implied by the deterministic wave equation of quantum mechanics.

The above result is very well known and appears to contradict the observation that adiabatic changes generally lead to an increase of entropy. The obvious conclusion, that information entropy can never be identified with thermodynamic entropy, is, however, totally erroneous. The correct conclusion is exactly the opposite. The demonstrated constancy of the uncertainty under the given conditions, far from contradicting the Second Law, is all that is required to prove an analogous law for maximised uncertainties.

This very surprising theorem is due to E.T. Jaynes\cite{18}. The point is that to define an uncertainty function identifiable with thermodynamic entropy we have to reject detailed knowledge of the intermediate non-equilibrium history of the body and use only the initial or final equilibrium measurements.\footnote{The one exception to the remarks of this paragraph occurs when the change is performed without friction and so slowly that the system remains effectively in equilibrium at all times. Any such process, and not only an adiabatic one, is called quasi-static and reversible. However, if the process is adiabatic, as well as quasi-static and reversible, then we are able to follow the intermediate evolution of the system by means of reproducible macroscopic measurements, for example, the pressure. This extra data is sufficient to ensure that the final maximised uncertainty $\sigma_{\text{max}}(F)$ is equal to the initial uncertainty $\sigma_{\text{max}}(I)$. The details of this important isentropic process will be elaborated in the next section, as part of the discussion of entropy change in an arbitrary quasi-static reversible process, one which may involve heat transfer in addition to work.} In particular, it is the maximised uncertainty determined by the final equilibrium data, alone, which represents the final thermodynamic entropy. The qualitative reason for the theorem is now easy to see. Indeed, it even seems trivial to remark that the maximal uncertainty...
consistent with the finally observed properties can not be less than any other information entropy compatible with the same data, and in general it must be greater. However, the remark is not entirely trivial because the final maximising probabilities refer to states which are different from the non-stationary evolved states \{\ket{\Psi_j^I(t_F)}\}. Hence the associated uncertainties are not directly comparable.

To see how this difficulty may be overcome we recall that the description of the final equilibrium should be given in terms of the eigenstates \{\ket{\varphi_m^F}\} of \hat{H}_F. We remember also that at equilibrium only the constant part of the expectation value of a reproducible observable effectively survives. So, if \(t_F\) is the time at which equilibrium has been reached, then for all \(t \geq t_F\)

\[
\langle \Psi_j^I(t) | \hat{Q} | \Psi_j^I(t) \rangle \approx \sum_m \langle \varphi_m^F | \hat{Q} | \varphi_m^F \rangle p(m(F) | j(I)).
\]  

(154)

Here, \(p(m(F) | j(I))\) is the probability of finding the state \(\ket{\varphi_m^F}\) when the system is known to be in the state \(\ket{\Psi_j^I(t)}\), the latter having evolved, under the action of \(\hat{H}(t)\), from the initial state \(\ket{\Psi_j^I(0)}\). For \(t \geq t_F\), \(\hat{H}(t)\) will by hypothesis have become the constant operator \(\hat{H}_F\) and at such times the state vector \(\ket{\Psi_j^I(t)}\) will satisfy the wave equation

\[
\hat{H}_F | \Psi_j^I(t) \rangle = i\hbar \frac{\partial | \Psi_j^I(t) \rangle}{\partial t}.
\]  

(155)

It follows that the \(a\)-coefficients in the expansion

\[
| \Psi_j^I(t \geq t_F) \rangle = \sum_m a[m(F) | j(I)] \ket{\varphi_m^F} \exp\left(-iE_m^F t / \hbar\right)
\]  

(156)

are constants, and that the required quantum probabilities are

\[
p(m(F) | j(I)) = | a[m(F) | j(I)] |^2.
\]  

(157)

Summation of these probabilities over \(m\) must yield unity since the states \{\ket{\varphi_m^F}\} are taken to be complete and orthonormal. Also, the square modulus of the \(a\)-coefficient can be interpreted in quantum theory as the probability \(p(j(I) | m(F))\) of finding \(\ket{\Psi_j^I(t \geq t_F)}\) when the state is known to be \(\ket{\varphi_m^F}\) \(\exp\left(-iE_m^F t / \hbar\right)\). Hence, by completeness and orthonormality the sum of the probabilities \(p(m(F) | j(I)) = p(j(I) | m(F))\) over \(j\) must be unity as well. In abbreviated notation, therefore,
these normalization conditions are
\[ \sum_m p(m|j) = 1 = \sum_j p(m|j). \]  
(158)

To complete the calculation of mean value estimates of observables we take into account that the evolved system states \(|\Psi_j^I(t)\rangle\) occur only with probabilities \(p(j|K_I)\). Thus at final equilibrium, when \(t \geq t_F\),
\[
\bar{Q}_F = \sum_j \langle \Psi_j^I(t) | \hat{Q} | \Psi_j^I(t) \rangle p(j|K_I) \\
\approx \sum_{m,j} \langle \varphi^F_m | \hat{Q} | \varphi^F_m \rangle p(m|j)p(j|K_I).
\]  
(159)

The above argument is clearly just a modification of the development in subsection (4.1) and the compounded probabilities in the expression for \(\bar{Q}_F\) may be treated by the same technique as given there. By Bayes’ theorem
\[
p(m|j)p(j|K_I) = p(m,j|K_I) = p(j|m.K_I)p(m|K_I),
\]  
(160)

and we derive immediately, by summation, the result
\[
\sum_j p(m|j)p(j|K_I) = p(m|K_I) \sum_j p(j|m.K_I).
\]  
(161)

Since the states \(|\Psi_j^I(t)\rangle\) are complete and orthonormal it follows at once that \(\sum_j p(j|m.K_I) = 1\).

Consequently, the mean value formula becomes
\[
\bar{Q}_F = \sum_m \langle \varphi^F_m | \hat{Q} | \varphi^F_m \rangle p(m|K_I),
\]  
(162)

where
\[
p(m|K_I) = \sum_j p(m|j)p(j|K_I)
\]  
(163)

may be interpreted as the probability of the occurrence of the final eigenstate \(|\varphi^F_m\rangle\) given the probabilities of the initial eigenstates \(|\Psi_j^I(0)\rangle\) and the details of the adiabatic process. Since \(\sum_m p(m|j) = 1\) and \(\sum_j p(j|K_I) = 1\), it is easy to see also that \(\sum_m p(m|K_I) = 1\).

We have now shown how to calculate the final equilibrium probability distribution over the appropriate energy eigenstates and can consider the implied information entropy. This is
\[
\sigma(F|I) = -\sum_m p(m|K_I) \ln (p(m|K_I)),
\]  
(164)
which in general is not the same as the maximised initial uncertainty given in terms of initial state probabilities by

$$\sigma_{\text{max}}(I) = -\sum_j p(j|K_I) \ln (p(j|K_I)). \quad (165)$$

The difference between them arises because of the quantum uncertainty inherent in the decomposition of the time-developed states \(\{|\Psi_j^I(t \geq t_F)\rangle\}\) into the final eigenstates \(\{|\varphi_m^F\rangle\}\) of \(\hat{H}_F\). A reasonable guess is that the initial uncertainty can not be decreased by this unavoidable quantum transition effect; but a formal proof is required. In summary, we have succeeded so far in identifying the correct *mechanically calculable* information entropy of the final equilibrium and now wish to show that

$$\sigma(F|I) \geq \sigma_{\text{max}}(I). \quad (166)$$

The proof of this basic result depends on the elementary inequality

$$x - 1 \geq \ln(x), \quad (167)$$

valid for \(x > 0\), and with equality only at \(x = 1\). The simplest way to see the truth of this relation is to draw the graphs of \(y = \ln(x)\) and its tangent \(y = x - 1\) at \(x = 1\), but of course an analytic derivation is easily constructed. Replacing \(x\) by \(1/x\) in the above equation we find quickly a further inequality which, written along with the first, yields

$$x - 1 \geq \ln(x) \geq 1 - 1/x, \quad (168)$$

again with the equality signs holding only for \(x = 1\). These simple relations form the basis for many proofs in information theory.

Using the definition of \(p(m|K_I)\), and the probability normalization conditions, we can write \(\sigma(F|I)\) and \(\sigma_{\text{max}}(I)\) in the forms

$$\sigma(F|I) = -\sum_{m,j} p(m|j)p(j|K_I) \ln (p(m|K_I)) \quad (169)$$

and

$$\sigma_{\text{max}}(I) = -\sum_{m,j} p(m|j)p(j|K_I) \ln (p(j|K_I)), \quad (170)$$
so that their difference becomes

\[
\sigma(F|I) - \sigma_{\text{max}}(I) = \sum_{m,j} p(m|j)p(j|K_I) \ln (p(j|K_I)) - \ln (p(m|K_I))
\]

\[
= \sum_{m,j} p(m|j)p(j|K_I) \ln \left( \frac{p(j|K_I)}{p(m|K_I)} \right)
\]

\[
\geq \sum_{m,j} p(m|j)p(j|K_I) \left[ 1 - \frac{p(m|K_I)}{p(j|K_I)} \right]
\]

\[
= \sum_{m,j} p(m|j)p(j|K_I) - \sum_{m,j} p(m|j)p(m|K_I)
\]

\[
= \sum_{j} p(j|K_I) - \sum_{m} p(m|K_I) = 0,
\]

\[
\Rightarrow \sigma(F|I) \geq \sigma_{\text{max}}(I),
\]

(171)

and we have proved the difficult intermediate result. The equalities in the above reasoning are either obvious mathematical transformations or follow from previously displayed normalization conditions, while the fundamental inequality is an instance of \(\ln(x) \geq 1 - 1/x\). This possible increase of uncertainty for a system with known evolution is a pure quantum effect and is usually negligible for macroscopic bodies.

To complete the proof and thus identify the origin of observable entropy increase we must show that \(\sigma_{\text{max}}(F) \geq \sigma(F|I)\). But now the trivial remark made earlier applies in its full triviality. The reason for this is that we have calculated the final mean values in the form

\[
\bar{Q}_F = \sum_m \langle \varphi^F_m | \hat{Q} | \varphi^F_m \rangle p(m|K_I),
\]

(172)

with associated entropy represented by

\[
\sigma(F|I) = - \sum_m p(m|K_I) \ln (p(m|K_I)),
\]

(173)

and have assumed that these computed \(\bar{Q}_F\) values would agree with direct experimental measurements, as summarised by the data \(K_F\) of the final equilibrium condition. On the other hand, a direct assignment of probabilities for the occurrence of the eigenstates \(\{|\varphi^F_m\}\), based on the same data values, would be done by maximising the uncertainty expression \(\sigma = - \sum_m q(m) \ln (q(m))\) subject to the constraints

\[
\bar{Q}_F = \sum_m \langle \varphi^F_m | \hat{Q} | \varphi^F_m \rangle q(m).
\]

(174)
By construction, the maximising distribution \( \{q(m|K_F)\} \) yields a value of the uncertainty, namely
\[
\sigma_{\text{max}}(F) = -\sum_m q(m|K_F) \ln(q(m|K_F)),
\]
which can not be less than the information entropy for any other distribution, such as \( \{p(m|K_I)\} \), which satisfies the same constraints. Therefore, we have proved quite generally that
\[
\sigma_{\text{max}}(F) \geq \sigma(F|I) \geq \sigma_{\text{max}}(I),
\]
for an adiabatic process connecting initial and final conditions of complete thermodynamic equilibrium.

This result is so important, and so central to a proper understanding of the statistical foundations of thermodynamics, that it is worthwhile to summarise the steps in the argument and the assumptions underlying them. The really fundamental hypothesis is that solution of the time-dependent Schrödinger equation will, in principle, enable accurate prediction of the future observables of a system when we know the probabilities of the various possible initial states. Those probabilities were found by maximizing the uncertainty function subject to the constraints implied by the initial Hamiltonian and the values of measured observables. It was then assumed that the evolution of each initial eigenstate could be calculated up to and beyond the time \( t_F \) at which equilibrium would again be established. The probabilities for these evolving states remain constant, but will presumably yield the experimentally observed final data. The initial information entropy thus also remains constant; in general, however, it does not correspond to the maximized uncertainty calculated using only the final Hamiltonian and measured data. The latter entropy would be relative to the final eigenstates, so we first show how to calculate an intermediate entropy greater than the initial one as a result of quantum transitions to final eigenstates. It then becomes obvious that this intermediate entropy must be less than the maximum uncertainty constructible from the same final data.
4.4 Composite systems

Two separate isolated bodies, each at equilibrium, may be regarded as a single equilibrated system with internal adiabatic and mechanical constraints, and it may be verified experimentally that the total energy is the sum of the energies of the subsystems. The bodies will also have separately measurable entropies. Now the total entropy $S$ can certainly be defined by the expression

$$S = S_1 + S_2,$$

(177)

but it is important to realise that total entropy $S$ can not be given a useful operational meaning independent of this definition so long as the bodies remain insulated from each other.

Additivity of thermodynamic entropy becomes an experimental proposition only when the adiabatic barrier is lifted and the bodies are allowed to exchange energy by heat transfer. At the same time the internal mechanical constraints may be wholly or partially removed so that one body can do macroscopically measurable work on the other. Under these conditions the energies and volumes of the subsystems will in general change; but, when mutual equilibrium has been achieved, it is usually observed that the bodies remain separately in equilibrium if contact between them is broken. It is thus reasonable to assume that bodies in a state of mutual equilibrium possess individually reproducible properties. The entropy of the compound system can then be calculated, as above, by adding the entropies of the constituent bodies. This is now an experimentally verifiable statement, and not just a definition, because the entropy of the total system can also be determined by global measurements and compared with the separately measurable entropies of the subsystems. The point of this discussion is that the principle of increase of thermodynamic entropy is used as a tool for predicting the final equilibrium state of a compound body whose parts can exchange energy. The eventual final state is taken to be the one of maximum total entropy as calculated from the sum of the entropies of the parts.

It is definitely implied in this account that we may attribute sharp intrinsic properties to the subsystems making up the composite body. We are postulating further that the total energy and
volume are themselves well represented experimentally by the sums

\[ \bar{E} = \bar{E}_1 + \bar{E}_2 \quad \text{and} \quad V = V_1 + V_2, \]  

which is equivalent to assuming that the coupling interaction between the bodies, and the region
over which it operates, are very small compared to the individual energies and volumes, respectively. The approximation is valid to a high degree of accuracy for macroscopic bodies interacting
by surface contact. Hence we are taking it as an observed fact that the empirical entropy of a
compound system formed from two bodies in mutual equilibrium is given by

\[ S(\bar{E} = \bar{E}_1 + \bar{E}_2, V = V_1 + V_2) = S_1(\bar{E}_1, V_1) + S_2(\bar{E}_2, V_2). \]  

A similar result holds if the two bodies can exchange matter as well as energy and volume. In
the simplest case both subsystems are made of the same kind of atoms and the total number of
atoms is given by \( N = N_1 + N_2 \). When the composite system is in a state of thermal, mechanical
and diffusive equilibrium it is found that

\[ S(\bar{E}, V, N) = S_1(\bar{E}_1, V_1, N_1) + S_2(\bar{E}_2, V_2, N_2), \]  

with an obvious generalisation if several kinds of atoms are present. It is also known empirically
that two bodies separately in equilibrium with a third will be in equilibrium with each other.
Thus the basic addition rule may be extended easily to a collection of more than two bodies, all
in mutual equilibrium.

The above generalisations support the proposition that the additive property of entropy holds
even for a single macroscopic body, thought of as conceptually divided into a large number of
macroscopic subsystems labelled by \( r = 1 \rightarrow R \). All the subsystems are individually in equilib-
rium and the body could, in principle, be physically separated into these parts by the insertion of
suitable barriers, assuming that the operation does not appreciably disturb the equilibrium condi-
tions. Explicitly, if the total entropy \( S = S(\bar{E}, V, N) \) is determined by the global data, and the
entropies of the parts are given by \( S_r = S_r(\bar{E}_r, V_r, N_r) \), in terms of the data for the subsystems,
then we can write

\[ S = \sum_r S_r, \quad \bar{E} = \sum_r \bar{E}_r, \]
\[ V = \sum_r V_r \quad \text{and} \quad N = \sum_r N_r. \]  

(181)

Now in order to compare entropy with the concept of maximal uncertainty, as applied to physical systems, the crucial point to grasp is that the thermodynamic entropy \( S_r \) of a subsystem is determined by the intrinsic data \( K_r = (\bar{E}_r, V_r, N_r) \) of that subsystem. It does not depend on the data \( K_s, s \neq r \), of any other subsystem. The data sets \( K_r, r = 1 \rightarrow R \), are not themselves independent of each other, since for fixed global data \( K \equiv (\bar{E}, V, N) \) we have the above sum-relations; but all inferences about the internal microscopic states of a given subsystem are to be assessed only on the corresponding data \( K_r \), and knowledge of any \( K_s \) with \( s \neq r \) is irrelevant. Thus we are free to consider each subsystem separately, with its own Hamiltonian, energy levels and data, and to construct an expression for the total uncertainty associated with a collection of such internally independent sub-problems.

In our physical applications the uncertainty is a function of the probabilities for the occurrence of possible energy eigenstates at equilibrium. We shall show generally that the additivity property of the uncertainty function is a purely mathematical result which is valid whenever the question at issue can be resolved into a set of independent statistical problems. This is not quite enough, however, to constitute a complete analogy with thermodynamic entropy, so we shall also need to discuss the conditions under which physical subsystems are in mutual equilibrium, and which ensure that the total uncertainty can be written as a function of the global summed data. These various aspects of additivity will be treated for the simple case of a composite body with two components, but the ideas are straightforwardly extendable. This apparently rather intricate treatment of additivity is necessary to establish firmly the parallels between uncertainty and entropy.

Consider first the uncertainties associated with two independent, problems, one having \( M \) possibilities \( \{A_m\} \), data \( K_A \), and uncertainty maximising probabilities \( \{p(A_m|K_A)\} \), the other
with \( N \) propositions \( \{ B_n \} \), data \( K_B \), and corresponding probabilities \( \{ q(B_n|K_B) \} \). In a mechanical application the propositions refer to energy eigenfunctions, e.g.,

\[
A_m = (\text{The eigenstate } |\varphi_m^A\rangle \text{ of Hamiltonian } \hat{H}_A \text{ occurs}).
\]

Assuming that each set of possibilities is internally exhaustive and mutually exclusive the assigned probabilities must satisfy the normalization conditions \( \sum_m p_m = 1 = \sum_n q_n \), and the individual maximised uncertainties are given by

\[
\sigma_{\text{max}}(K_A) = - \sum_m p_m \ln (p_m) \quad \text{and} \quad \sigma_{\text{max}}(K_B) = - \sum_n q_n \ln (q_n).
\]

Now construct a compound problem by forming all conjunctions \( (A_m,B_n) \) considered on evidence \( (K_A,K_B) \). Such compound propositions are also exhaustive and mutually exclusive if the evidence and inferences in one sub-problem are irrelevant to inferences in the other. This constitutes the condition of independence. The joint probabilities are

\[
P(A_m,B_n|K_A,K_B) = P_{mn}, \quad \text{with} \quad \sum_{m,n} P_{mn} = 1,
\]

and the total information entropy takes the form

\[
\sigma(K_A,K_B) = - \sum_{m,n} P_{mn} \ln (P_{mn}).
\]

But, by Rule(1) of subsection (3.3) we know that

\[
P(A_m,B_n|K_A,K_B) = P(A_m|B_n,K_A,K_B)P(B_n|K_A,K_B),
\]

which, from the stated condition of independence, reduces to

\[
P_{mn} = p(A_m|K_A)q(B_n|K_B) = p_m q_n.
\]

It is now easy to see that we may derive the simple result

\[
\sigma(K_A,K_B) = - \sum_{m,n} p_m q_n \ln (p_m q_n)
\]

\[
= - \sum_{m,n} p_m q_n [\ln (p_m) + \ln (q_n)]
\]

\[
= - \sum_m p_m \ln (p_m) - \sum_n q_n \ln (q_n)
\]

\[
= \sigma_{\text{max}}(K_A) + \sigma_{\text{max}}(K_B).
\]
All we have shown so far is that the total uncertainty $\sigma(K_A.K_B)$ associated with two arbitrary bodies, each in a condition of internal equilibrium, is represented by the sum of the maximised uncertainties $\sigma_{\text{max}}(K_A)$ and $\sigma_{\text{max}}(K_B)$ of the separate isolated systems. There is no implication that $\sigma(K_A.K_B)$ is the same as the maximised uncertainty $\sigma_{\text{max}}(K)$ which would follow from a knowledge of the summed data $K = [\bar{E}, V]$, where $\bar{E} = \bar{E}_A + \bar{E}_B$ and $V = V_A + V_B$, and indeed this would not be true in general.

The situation is different, however, if the bodies are in thermal and mechanical contact and have come into mutual equilibrium, but are otherwise isolated from external influences. The resulting composite body may be regarded as a single system, in total internal equilibrium, having a maximal uncertainty determined by the summed data. By construction, this maximised uncertainty can not be less than any other uncertainty which has been calculated from alternative probabilities consistent with the same summed data. The implication now is that the two subsystems will take up energies and volumes consistent with the known sums, but also constrained by the condition of mutual equilibrium. If they were not in equilibrium when first placed in contact then the small coupling interaction between them would initiate an adiabatic process inside the composite body which would continue until equilibrium was attained. By the results of the last subsection the final maximised uncertainty can not be less than the initial uncertainty and will in general be greater. Since, moreover, we have assumed that the subsystems will still have independent uncertainties determined by the final equilibrium data $K_A$ and $K_B$, we see that, for consistency, the maximised total uncertainty at mutual equilibrium must be represented by

$$\sigma_{\text{max}}(K) = \sigma_{\text{max}}(K_A) + \sigma_{\text{max}}(K_B).$$

(189)

It is clear from the above discussion that the additivity of maximised information entropy, under the given conditions, is a direct deduction from the basic dynamical result that maximal uncertainty is not decreased by an adiabatic process. We have also made essential use of the qualitative knowledge that the composite body is made from two subsystems with independently constructible uncertainties. The maximal uncertainty implied by the summed data is attained
when the subsystems reach mutual equilibrium with definite partitioning of the total energy and volume. We see immediately that the addition rule for maximised uncertainties becomes a powerful tool for predicting the conditions of mutual equilibrium between bodies.

Suppose, for example, that we know the total energy \( \bar{E} = \bar{E}_A + \bar{E}_B \) and total volume \( V = V_A + V_B \) of two isolated bodies, each at equilibrium, and also their maximised uncertainties, \( \sigma_{\text{max}}(\bar{E}_A, V_A) \) and \( \sigma_{\text{max}}(\bar{E}_B, V_B) \), as functions of the respective data. If the bodies remain in equilibrium when placed in thermo-mechanical contact then the uncertainty of the resulting composite system, namely

\[
\sigma(\bar{E}, V) = \sigma_{\text{max}}(\bar{E}_A, V_A) + \sigma_{\text{max}}(\bar{E}_B, V_B),
\]

must also be maximal for the summed data. Assuming that \( \bar{E} = \bar{E}_A + \bar{E}_B \) and \( V = V_A + V_B \) are fixed at given values it follows at once that conditions for mutual equilibrium may be expressed by the maximising relations

\[
\frac{\partial \sigma_{\text{max}}}{\partial \bar{E}_A} = \frac{\partial \sigma_{\text{max}}}{\partial \bar{E}_B} \quad \text{and} \quad \frac{\partial \sigma_{\text{max}}}{\partial V_A} = \frac{\partial \sigma_{\text{max}}}{\partial V_B}. \tag{191}
\]

We have here a natural extension of the principle of maximum information entropy which shows how \( \sigma_{\text{max}}(K) \) yields definite criteria for equilibrium between interacting bodies. Since the empirically determined entropy \( S \) is used in exactly the same way for prediction of the values of macroscopic observables of bodies in mutual equilibrium, the analogy between these theoretical and experimental quantities is greatly strengthened. The corresponding relations for \( S \) are

\[
\frac{\partial S_A}{\partial \bar{E}_A} = \frac{\partial S_B}{\partial \bar{E}_B} \quad \text{and} \quad \frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \tag{192}
\]

which are well known to express, respectively, equality of temperature and pressure in the two systems. Thus a successful identification of \( \sigma_{\text{max}}(K) \) with \( S \) opens up the possibility of a statistical interpretation of temperature.

### 4.5 Meaning of entropy

The results of the last few subsections establish the existence of a theoretical quantity, \( \sigma_{\text{max}}(\bar{E}, V, N) \), which has some of the characteristic properties of thermodynamic entropy \( S \). It depends explicitly
on the data at equilibrium and on the Hamiltonian of the system, and is a direct measure of our uncertainty about the exact state of the body. The really vital assumption in the demonstrations was that calculated mean values of observables would agree with experimental measurements of the observables. This postulate provided the necessary link between the mathematical properties of $\sigma_{\text{max}}$ and possible processes in physical systems. The empirical entropy, $S(\bar{E}, V, N)$, on the other hand, is found, up to an arbitrary additive constant, entirely from observations of energy and temperature changes in quasi-static, reversible processes, and requires no knowledge of the internal structure of the body. Hence, for logical completeness, we should show that the function $\sigma_{\text{max}}(\bar{E}, V, N)$ can be determined in the same way, apart from a corresponding arbitrary constant. However, it is convenient to defer this clinching step in the identification of $S$ with $\sigma$ to the next section.

It is, nevertheless, already plausible that the thermodynamic and statistical functions are closely related and that the theoretical interpretation gives a definite meaning to the usual remark that entropy is a measure of disorder in the system. More precisely, the disorder is not in the system, which is always in some particular quantum state, but in our knowledge about the system. The available data are insufficient to specify the actual state and we are forced to use probabilistic inference. The uncertainty function then provides a means for estimating probabilities and its maximised value is a natural measure of our state of doubt. The uncertainty can only be made smaller by acquiring more data. The truly surprising thing is that just a little information, supplemented by efficient guesswork, can lead to accurate prediction of reproducible observations.

Although a full justification has not yet been given, we now make the working hypothesis that thermodynamic entropy and maximised uncertainty are essentially equivalent representations of our lack of knowledge about the actual state of a body. Writing $\sigma_{\text{max}} = \sigma$ for brevity, we assume

$$S = f(\sigma),$$  \hspace{1cm} (193)

where $f(\sigma)$ must be a monotonic increasing function of $\sigma$ since both $S$ and $\sigma_{\text{max}}$ are non-decreasing in adiabatic processes. Also, because $S$ and $\sigma_{\text{max}}$ are both additive for interacting but effectively
independent systems at mutual equilibrium, we must have, for two such bodies, that

\[ S = S_1 + S_2 \quad \text{and} \quad \sigma = \sigma_1 + \sigma_2, \tag{194} \]

which leads immediately to the functional equation

\[ f(\sigma_1 + \sigma_2) = f(\sigma_1) + f(\sigma_2), \tag{195} \]

to be satisfied by \( f(\sigma) \). Differentiating successively with respect to \( \sigma_1 \), and \( \sigma_2 \), we find quickly that

\[ f'(\sigma_1 + \sigma_2) = f'(\sigma_1) = f'(\sigma_2) = k_B, \tag{196} \]

where \( k_B \) is a positive constant. Integration then gives

\[ S = f(\sigma) = k_B \sigma_{\text{max}}(\bar{E}, V, N) + S_c, \tag{197} \]

with \( S_c \) an arbitrary constant.

This result should be compared with a slightly expanded version of the formula already given for the expression of thermodynamic entropy in terms of experimental data, namely

\[ S = S_{\text{exp}}[(\bar{E}, V, N), (\bar{E}_0, V_0, N_0)] + S_0 \tag{198} \]

in which \( S_0 \) is an arbitrary constant.

The quantity \( S_{\text{exp}}(K, K_0) \), where \( K \) and \( K_0 \) stand for the data sets, is determined from definitely prescribed experimental operations on the system, which take it from a reference condition \( K_0 \) to the final equilibrium \( K \). If we now write our theoretical interpretation of \( S \) in the rearranged form

\[ S = k_B[\sigma_{\text{max}}(K) - \sigma_{\text{max}}(K_0)] + [S_c + k_B\sigma_{\text{max}}(K_0)], \tag{199} \]

and choose the arbitrary constants \( S_0 \) and \( S_c \) such that

\[ S_0 = S_c + k_B\sigma_{\text{max}}(K_0), \tag{200} \]

then the experimental entropy relative to \( K_0 \) may be identified as

\[ S_{\text{exp}}(K, K_0) = k_B[\sigma_{\text{max}}(K) - \sigma_{\text{max}}(K_0)]. \tag{201} \]
The one remaining gap in our arguments is that we have not shown that the differential relations underlying the experimental procedures for measuring $S_{\text{exp}}$ are the same as those describing the changes of $k_B \sigma_{\text{max}}$ during such operations. The missing demonstration necessarily involves an explanation of the statistical meaning of temperature, together with an identification of $k_B$ as Boltzmann’s constant. When this has been achieved the derivation of thermodynamics from statistical mechanics will be essentially complete. The proof will be given after the appropriate probability distributions have been derived.

We conclude this subsection by remarking that the experimental entropy $S_{\text{exp}}$ would have an absolute significance if we could measure it relative to a condition $K_0$ for which the maximised uncertainty is either zero or a characteristic structural constant for the given system. The uncertainty could be zero only if the data $K_0$ are such that we know the exact state of the body, but we have argued that this is generally impossible. An exception would occur, however, if the measured energy, identified with the theoretical mean value $\bar{E}_0$, were equal to the ground state energy $E_G$ of the system. The body must then be in its ground state and, if the state is non-degenerate, the associated uncertainty would vanish. It is believed that the ground states of all real physical systems are in fact non-degenerate; but, if the lowest level should happen to comprise $\Omega_0$ degenerate states, as it does in some simplified theoretical models, the uncertainty would by $\ln (\Omega_0)$. This latter value is almost always found to be independent of macroscopic mechanical parameters such as the volume. Thus, provided the body remains in its ground level, externally imposed alterations of the system configuration will not change the uncertainty. The previous probabilistic considerations would then be unnecessary. The body may be treated as a pure mechanism whose properties are calculable, in principle, by the standard techniques of quantum theory.

For any other equilibrium condition specified by data $K \equiv (\bar{E}, V, N)$ it now seems reasonable to represent the thermodynamic entropy as an absolute quantity by writing

$$S(\bar{E}, V, N) = k_B \sigma_{\text{max}}(\bar{E}, V, N),$$

with the implication that, as $\bar{E}$ approaches the ground state energy $E_G$ the entropy $S$ tends to
zero or to a constant which is independent of the mechanical parameters. This is the Third Law of Thermodynamics. It will be shown later that $\bar{E}$ can equal $E_G$ only at the absolute zero of temperature, which is in practice unattainable, but can be approached very closely. Hence a good approximation to absolute entropy can often be determined by starting with the system at a very low temperature. The value of $S(\bar{E}, V, N)$ found subsequently, from thermal experiments, may then sometimes be compared with an independent measurement of $k_B \sigma_{\text{max}}(\bar{E}, V, N)$ using structural data obtained spectroscopically. Such comparisons can yield valuable information.

Development of the implications of the Third Law in physics and physical chemistry and discussions of its experimental status are well beyond our scope. The whole topic of physics at very low temperatures is extremely intricate and involves delicate decisions about whether or not the body being investigated can be considered to be in equilibrium. Some degrees of freedom may be frozen into metastable states whose evolution towards equilibrium is hampered by potential energy barriers. The application of thermodynamics to such systems is problematical. It is sometimes claimed that the Third Law explains the observed decrease of quantities such as thermal heat capacities at the low temperatures reachable by experiment, but modern analyses require more information on $S(\bar{E})$ as $\bar{E}$ approaches $E_G$. 

5 Entropy and temperature

5.1 Constrained maximization

We have now shown, pending an investigation of how uncertainty can be measured directly, that
\[ \sigma_{\text{max}}(\bar{E}, V, N) \] has all the vital properties of the thermodynamic entropy \( S(\bar{E}, V, N) \). Hence, on
using the physical principle that statistical estimates of reproducible observables will agree with
experimental measurements, the two quantities may be related by writing

\[ S(\bar{E}, V, N) = k_B \sigma_{\text{max}}(\bar{E}, V, N), \] (203)

where \( k_B \) is a constant depending on the measurement units.

This proposed identification of the theoretical quantity \( \sigma_{\text{max}} \) and the phenomenological \( S \)
greatly simplifies the conceptual development of statistical mechanics. In particular, the absolute
temperature \( T \) can be introduced into the formalism by using the traditional thermodynamical arg-
ments involving the Second Law. Such treatments show that \( 1/T \) is an integrating factor for the
differential of heat transfer and is equal to the partial derivative \( \partial S/\partial \bar{E} \). The above formula then
indicates that \( T \) is derived from theory by means of the relation \( \partial \sigma_{\text{max}}/\partial \bar{E} = 1/(k_B T) \). Further
discussion of these matters requires an explanation of how to calculate the absolute maximum of
the information entropy \( \sigma = - \sum_j p_j \ln (p_j) \), and the corresponding probability distribution \( \{p_j\} \),
in terms of the assumed data \( K = (\bar{E}, V, N) \). The result will be an explicit theoretical expression
for the thermodynamic entropy, built up from a knowledge of the microscopic constitution of the
system and the values of the measured data.

We start on this by considering the general problem of constrained maximisation, which may
be formulated as follows. Given that there are \( M \) variables \( \{x_j\}, \ j = 1 \rightarrow M \), it is required to
find the absolute maximum of a function

\[ F(x_1, \ldots, x_j, \ldots, x_M), \] (204)

and the corresponding set of maximising values of the variables \( \{x_j\}_{\text{max}} \), when the allowed \( x \)'s
must always satisfy the \( n \) constraint equations

\[ G_\alpha(x_1, \ldots, x_j, \ldots, x_M) = g_\alpha, \] (205)
with $\alpha = 1 \to n$, $n < M$ and the $g_\alpha$’s a set of fixed numbers.

Now for a fully satisfactory solution of the problem, as it arises in statistical physics, we must certainly do two things:

- 1) somehow derive a proposed solution, and
- 2) prove that it is the absolute maximum.

The second part of the demonstration is omitted in most accounts of the calculation, but is really necessary for logical completeness since the usual variational techniques do not ensure that the absolute maximum has been attained. It appears in our particular problem that the variational method, using Lagrange Multipliers, does in fact provide an elegant and correct solution; but it is still of some interest that a relatively simple proof of this fact can be given which exploits the special form of the uncertainty function. The idea of this proof will be explained in the next subsection after the canonical probability distribution of thermal physics has been derived.

To return to the general problem set out above we proceed by considering small variations $\delta x_j$ in the $x_j$’s and calculate the associated variation $\delta F$ of the function $F$. This variation must certainly vanish at any smooth maximum of $F$ and thus a necessary condition to be satisfied by $F$ at such a point, for small, but to a large extent, arbitrary $\delta x_j$, is given by

$$\delta F = \sum_j \left( \frac{\partial F}{\partial x_j} \right) \delta x_j = 0. \tag{206}$$

If there were no subsidiary equations constraining the allowable variations of the $\{x_j\}$ then we could argue as follows. Since the $\delta x_j$ may be chosen independently and arbitrarily, we can set all but one of them, say $\delta x_k$, equal to zero and hence derive the condition $(\partial F/\partial x_k) \delta x_k = 0$ to be satisfied for any small value of $\delta x_k$. Clearly this can hold only if the partial derivative is zero. Extension of the argument to all the $\delta x_j$ then shows that at a smooth maximum of $F$ or, indeed, at any smooth extreme point of the function, we must have

$$\frac{\partial F}{\partial x_j} = 0, \quad j = 1 \to M. \tag{207}$$
Investigation of the exact nature of the extrema thus determined usually requires computation of the second derivatives also, but even when this is done it may still prove difficult to pick out the absolute maximum.

The argument just given breaks down when the constraint conditions are imposed since the variations $\delta x_j$ can no longer be taken to be arbitrary, but must be related by the $n$ equations ($\alpha = 1 \rightarrow n$)

$$\delta G_\alpha = \sum_j \left( \frac{\partial G_\alpha}{\partial x_j} \right) \delta x_j = 0.$$  

(208)

We could at this point just use these equations to eliminate $n$ of the $\delta x_j$ from the expression for $\delta F$ and then, by the same type of process as above, vary the others arbitrarily so as to obtain $(M - n)$ equations connecting the variables at an extremum. Taking into account the $n$ constraints $G_\alpha = g_\alpha$ themselves, we would thus have enough equations to determine the extremising values of the $\{x_j\}$, at least in principle. It is, however, mathematically more elegant and, physically, much more convenient to introduce instead certain auxiliary constants $\lambda_\alpha$ known as the Lagrange Multipliers, one for each of the constraint equations. Every such condition is multiplied by a corresponding $\lambda_\alpha$ and the results added together and to the variation $\delta F$ to yield the equation:

$$\delta F + \sum_\alpha \lambda_\alpha \delta G_\alpha = \sum_j \left[ \frac{\partial F}{\partial x_j} + \sum_\alpha \lambda_\alpha \left( \frac{\partial G_\alpha}{\partial x_j} \right) \right] \delta x_j = 0.$$  

(209)

Now the so far undetermined constants $\lambda_\alpha$ are at our disposal and we are free to choose them so that the coefficients $(\partial F/\partial x_j) + \sum_\alpha \lambda_\alpha (\partial G_\alpha/\partial x_j)$ of $n$ of the $\delta x_j$ are zero. The remaining $(M - n)$ of the $\delta x_j$ may then be varied independently and arbitrarily as in the process for unconstrained extremisation given above. We could, for example, choose them all zero except for $\delta x_k$, say, so that we arrive at the variational condition

$$\left[ \frac{\partial F}{\partial x_k} + \sum_\alpha \lambda_\alpha \left( \frac{\partial G_\alpha}{\partial x_k} \right) \right] \delta x_k = 0,$$  

(210)

which can be satisfied for arbitrary $\delta x_k$ only by having the coefficient of $\delta x_k$ equal to zero. The result of a systematic application of this new method is the set of $(M + n)$ equations

$$\frac{\partial F}{\partial x_j} + \sum_\alpha \lambda_\alpha \left( \frac{\partial G_\alpha}{\partial x_j} \right) = 0, \quad j = 1 \rightarrow M,$$  

(211)

$$G_\alpha(\{x_j\}) - g_\alpha = 0, \quad \alpha = 1 \rightarrow n,$$  

(212)
which determines the \((M + n)\) unknowns \(x_1, \ldots, x_M; \lambda_1 \ldots, \lambda_n\).

This analytical method is very powerful when applied in statistical mechanics, as we shall see, but we must also take note of the potential problems. There will in general be many different solutions to the above equations other than the one corresponding to the greatest maximum that we seek; they will give rise to lesser maxima, or to minima, or to complicated saddle points of the function \(F\). The differential technique may even miss the absolute maximum altogether if it occurs at a point where \(F\) has some cusp-like shape with no well defined derivatives. Thus when a “solution” has been generated it is certainly necessary to convince oneself that it corresponds to the highest value of \(F\).

To conclude this subsection we apply the above mentioned method to the simple case of an isolated body which has \(N\) particles in volume \(V\) and an energy \(\bar{E}\) known to be in the interval from \(E\) to \(E + \Delta E\). As before, we suppose that the Hamiltonian \(\hat{H}(V,N)\) can be constructed and that the eigenstates \(\psi_j(V,N)\), and corresponding energy eigenvalues \(E_j(V,N)\), of the body can be found. We can thus calculate the number \(\Omega = \Omega(\bar{E}, V, N)\) of accessible states whose energies obey the condition \(E < E_j < E + \Delta E\) and we wish to make an honest assessment of the probabilities \(\{p_j\}\) with which these states occur. This is precisely the problem that we solved by common sense in section 2 and by an invariance argument in section 3; it is to be hoped that the third method will give the same answer, namely, that the probabilities for the accessible states are all equal to \(1/\Omega\). We also wish to prove, of course, that this solution corresponds to the absolute maximum of the uncertainty or information entropy function.

Assuming that the \(\Omega\) accessible energy eigenstates are orthogonal and are labelled by \(j = 1 \rightarrow \Omega\) we require to find the probabilities \(\{p_j\}\) of these states by maximising the uncertainty function

\[
\sigma = -\sum_j p_j \ln (p_j),
\]

subject to the constraint

\[
\sum_j p_j = 1,
\]

which expresses that the accessible states form a set of exhaustive and mutually exclusive possi-
bilities, i.e., that exactly one of them occurs.

Varying the \( \{p_j\} \), and setting the induced variation of \( \sigma \) to zero, gives

\[
- \delta \sigma = \sum_j [1 + \ln (p_j)] \delta p_j = 0,
\]

in which the allowed variations are restricted by the condition

\[
\sum_j \delta p_j = 0.
\]

(215)

(216)

Multiplying the latter variational equation by a constant \( \alpha \) and adding it to the former one now yields the combined equation

\[
\sum_j [\alpha + 1 + \ln (p_j)] \delta p_j = 0,
\]

in which the coefficients of the \( \{\delta p_j\} \) can, by the arguments above, be all equated to zero. Hence for all \( j \) we find easily that \( p_j = \exp (-\alpha - 1) \), and application of the probability normalisation constraint on the \( \Omega \) possible states then leads to the previous result

\[
p_j = \frac{1}{\Omega}, \quad j = 1 \to \Omega.
\]

(217)

(218)

We already know from subsection 3.5 that if, consistently with the constraints, we can make any pair of probabilities more equal, then the value of the uncertainty function will increase. Since, in the above problem, the probabilities are derived to be all equal, the absolute maximum of the \( \sigma \)-function must have been attained, namely, \( \ln [\Omega(E,V,N)] \).

5.2 Canonical probabilities

We are now in a position to derive the probability distribution over energy eigenstates for a body subjected to the experimental conditions most commonly encountered in thermal physics. Since these conditions are overwhelmingly the most usual ones, the corresponding probabilities are called canonical. The simple final formula for the probability of occurrence of some particular energy eigenstate may be regarded as the central result in the standard form of statistical mechanics. Once this formula has been established, all the preceding framework of probability and uncertainty theory can essentially be disregarded; work can then be concentrated on understanding, and
modelling, the mechanics of various individual systems and attempting to evaluate the sums over states that arise from the canonical treatment. Most modern research and teaching in statistical physics does in fact take this line, to all intents assuming the probability formula as an axiom; but much greater understanding, and confidence in the results, can be achieved by making some effort to appreciate the purely inferential nature of the fundamental formula. It is, of course, essential to do this before generalisations of the theory can safely be undertaken. We will eventually derive a minor extension of the canonical method, mainly for computational reasons; but the point is that this is easy to do when the probabilistic background is understood. It is not necessary to invent a new axiom. The underlying probability methods may also be applied to give formalisms appropriate for other static experimental conditions and even for non-equilibrium situations.

The canonical form of equilibrium statistical mechanics is designed to describe the properties of a system for which, not the energy, but the temperature is known. The concept of temperature arises in a natural way from the reproducible observation of spontaneous energy transfer between bodies placed in loose energy contact. Such a process occurs in general even when the two bodies are themselves both in equilibrium initially. Systems in thermal contact eventually come to a mutual equilibrium and then each remains in equilibrium when separated from the other. Hence it is possible to start with two separately equilibrated systems, allow them to exchange energy by thermal contact, and finally to separate them again as two mutually and internally equilibrated bodies. The body which loses energy in this type of process is said to be hotter than the other and two bodies which remain in their initial equilibrium states when placed in thermal contact are said to be equally hot. The primitive notion is the idea of equal hotness and it is desired experimentally to construct a reproducible scale for measuring the hotness of bodies so as to determine easily if two or more systems will be in mutual equilibrium when placed in thermal contact. The usual procedure is to choose some standard body, with a readily measurable, hotness-dependent property, to act as a thermometer. If the thermometer gives the same readings when in thermal equilibrium with two separate bodies, then this may be taken to imply that the two measured systems would also be in mutual equilibrium if placed in thermal contact. The systems are now
said to be at the same temperature. There are many physical properties suitable as thermometric indicators for which no ambiguities arise in the assignment of equal hotness to bodies.

It is also found experimentally that the readings of thermometers may be used to judge the relative hotness of bodies; which is to say that these readings may be ordered so that, for example, the values observed for the temperatures of two different bodies can be correlated unambiguously with the direction in which net energy transfer occurs when the bodies are allowed to equilibrate with each other. The development of accurate thermometers is a highly technical subject which we will not go into. We wish only to draw attention to the fact that there is a reproducibly measurable property of systems, the temperature, which controls the net spontaneous exchange of energy between coupled systems, each initially in equilibrium. The real nature of this quantity is somewhat obscure in macroscopic thermodynamics, but since it is connected with net energy transfers there are strong indications that it is basically statistical. It was eventually discovered to be possible to set up a universal or absolute scale of temperature, denoted by $T$, which is independent of the properties of particular substances, such that greater hotness always corresponds to greater $T$. This will be discussed in more detail in the next subsection, but it is worth remarking here that the really important feature of $T$ is that all thermodynamic relations between measurable properties of systems are valid only when the absolute scale is used.

Historically and logically in the development of thermal physics the concept of absolute temperature was bound up inextricably with the idea of entropy. Our purpose now is to show that application of the formalism of maximal uncertainty also implies a universal scale for a parameter of systems which orders the hotness of isolated bodies, each in a state of internal equilibrium. That is, we shall show for such systems that there exists a quantity, calculable in principle from mechanics, corresponding to absolute temperature. Although for most bodies the parameter has a very complicated expression in terms of the mechanical specifications, its value is the same for two systems which remain in equilibrium when brought into thermal contact. Further, its values, for two bodies which do not remain in equilibrium on establishment of thermal contact, enable the direction of spontaneous energy exchange to be inferred. Thus it has the operational features
of temperature and its importance lies in the fact that it may be found experimentally without a
detailed knowledge of internal dynamics. The possibility of such direct measurement depends in
an essential way on how uncertainty may be determined experimentally from macroscopic infor-
mation. This will be explained later.

We turn now to the derivation of canonical probabilities for occurrence of energy eigenstates
in a body known to be in equilibrium, on the basic assumption that the system possesses a
reproducibly measurable average energy. A constant mean energy $\bar{E}$ certainly exists for any
isolated body, even if it is not in equilibrium, as we showed in section 2, but is also observed for
an equilibrated body which is thermally coupled to another, much larger system (or heat bath),
itself in equilibrium. In the latter situation it is found that although repeated measurements of
the energy of the body may show small fluctuations, there is a very sharply defined mean value
which may also be taken as an estimate of the energy when the body is removed from contact with
the heat bath. The important point is that the body does not show any systematic tendency to
exchange energy with the bath. Such considerations, of course, underlie our preliminary discussion
of the temperature concept and in practice what is really measured is the temperature of the body;
but it is not possible at this stage to introduce that concept directly. We shall see later, however,
that for any specific body a given average energy $\bar{E}$ implies a definite temperature and vice
versa. Still, the mean energy is a measurable thing and it is certainly allowable to investigate
the form of the eigenstate probabilities on the basis of given mean system energy $\bar{E}$, together
with specification of the volume $V$, the number of particles $N$ and the system Hamiltonian. The
connection between energy and temperature then emerges naturally from the formalism and the
subsequent description of how the maximised uncertainty can be found by experiment (this gives
the usual thermodynamic entropy) also indicates how the temperature parameter of the body can
be measured and inserted directly into the final formulae.

Thus we now consider a body, either isolated, or in loose energy contact with a heat bath, to
which can be attributed a quite sharply defined mean energy $\bar{E}$. We do not assume the artificial
condition of the microcanonical method that the energy is definitely known to be in a small
interval from $E$ to $E + \Delta E$ and hence we can no longer claim that there is only a finite number of possibilities for the exact eigenstate. Instead, we must now envisage that any energy eigenstate has some probability of occurrence. This implies that at the end of every particular application of the new method we should certainly check that the expected deviations from the assigned mean energy are indeed small, i.e., that the energy of the system is a sharply defined and therefore reproducible quantity in accord with experiment.

We assume as before that the Hamiltonian $\hat{H}(V,N)$ of the system is known and that the eigenstates $\psi_j(V,N)$ belonging to eigenvalues $E_j(V,N)$ can be constructed. The index $j$ represents all the quantum numbers required to distinguish the energy eigenstates from each other, so that states which are degenerate in energy are also separately labelled. Given the mean energy $\bar{E}$ of the body at equilibrium, we can now straightforwardly assign probabilities for the occurrence of the energy eigenstates by maximising the uncertainty function

$$\sigma = -\sum_j p_j \ln (p_j),$$

subject to the constraint equations

$$\sum_j p_j = 1 \quad \text{and} \quad \sum_j p_j E_j(V,N) = \bar{E},$$

which symbolise that the states form a set of exhaustive and mutually exclusive possibilities and that the average energy is specified. Varying the $\{p_j\}$, and setting the implied variation of $\sigma$ to zero, yields

$$-\delta\sigma = \sum_j [1 + \ln (p_j)]\delta p_j = 0,$$

which is satisfied under the variational restrictions

$$\sum_j \delta p_j = 0 \quad \text{and} \quad \sum_j \delta p_j E_j(V,N) = 0.$$

Multiplying the two last equations respectively by $\alpha$ and $\beta$ and adding them to the previous one results in the combined equation

$$\sum_j [\alpha + 1 + \beta E_j(V,N) + \ln (p_j)]\delta p_j = 0,$$
in which, by previous arguments, the bracketed coefficients of the \( \{ \delta p_j \} \) can all be equated to zero. Hence we deduce that, for all \( j \),

\[
p_j = \exp (-\alpha - 1) \exp [-\beta E_j(V, N)]. \tag{224}
\]

We see therefore that the probability of occurrence of the state \( \psi_j(V, N) \) depends only on the energy eigenvalue \( E_j(V, N) \) of that state and on the fixed, but so far undetermined, parameters \( \alpha \) and \( \beta \).

The factor \( \exp (-\alpha - 1) \) is quickly reducible to a useful form by inserting the last equation into the normalisation condition, which gives us at once that

\[
\sum_j p_j = 1 = \exp (-\alpha - 1) \sum_j \exp [-\beta E_j(V, N)]. \tag{225}
\]

Equation (224) can thus be rewritten as

\[
p_j = \frac{\exp [-\beta E_j(V, N)]}{Z(\beta, V, N)}, \tag{226}
\]

where

\[
Z(\beta, V, N) = \sum_j \exp [-\beta E_j(V, N)]. \tag{227}
\]

By this manipulation the probability normalisation condition is made manifest. The, at first sight, trivial normalisation factor \( Z \) above actually plays a central rôle in all subsequent developments of the canonical method and is called the partition function or, sometimes, the sum-over-states. It is a function of \( \beta \) and mechanical parameters.

Having eliminated the explicit appearance of \( \alpha \) in the formalism, we may attempt a similar exercise for \( \beta \). However, it is not possible to do this in general; nor is it even desirable, since \( \beta \) proves to be important in its own right. It is a statistical parameter that is closely related to the mean energy \( \bar{E} \), itself an intrinsically statistical quantity, though determinable, of course, by measurement. The required connection is easily derived by inserting the probabilities above into the second form of the normalisation condition; this leads to the sequence of equalities

\[
\bar{E} = \sum_j p_j E_j = \frac{\sum_j \exp [-\beta E_j(V, N)] E_j(V, N)}{Z(\beta, V, N)}
\]

\[
= - \left( \frac{1}{Z} \right) \frac{\partial \sum_j \exp [-\beta E_j]}{\partial \beta} = - \left( \frac{1}{Z} \right) \frac{\partial Z}{\partial \beta}, \tag{228}
\]
from which we deduce the crucially important equation
\[ \bar{E} = -\frac{\partial \ln [Z(\beta, V, N)]}{\partial \beta}. \] (229)

Regarded as an equation for determining \( \beta \) from assumed information about \( \bar{E} \), the above Eq.(229) does not seem at all satisfactory, since it generally implies a complicated transcendental relation for \( \beta \) as a function of \( \bar{E} \). But in every application it is much more convenient to have \( \bar{E} = \bar{E}(\beta) \), as in Eq.(229), the reason being that \( \beta \) is a simple function of the absolute temperature of the system and is much easier to measure. The theoretical importance of this equation is to show that knowledge of \( \beta \) is equivalent to a specification of \( \bar{E} \) and may be used to replace that assumed input for the assignment of probabilities. The extremely pleasant outcome is that the very accurately measurable temperature of a body enters, via its simple and unique relation to \( \beta \), directly into the formulae (226) and (227) for the canonical probabilities. One of the beautiful and surprising features of the variational method is that quantities originally introduced just for mathematical convenience frequently assume direct physical significance. We will soon show that \( \beta \) is in fact proportional to the reciprocal of the absolute temperature \( T \) so that Eq.(226) can be construed as giving the state probabilities implied by knowledge of \( T \), rather than of \( \bar{E} \), as we assumed at the start. But before moving on to this we give the simple proof that, under the given constraints, the variationally derived probabilities do yield the absolute maximum of the uncertainty function.

We use Eq.(226) for the canonical probabilities and recall the inequality employed in section 4, namely \( \ln (x) \leq x - 1 \), with equality holding only when \( x = 1 \). Consider now any other probability distribution \( \{q_j\} \) for the energy eigenstates, which satisfies the same constraint equations, i.e.,
\[ \sum_j q_j = 1 \quad \text{and} \quad \sum_j q_j E_j(V,N) = \bar{E}. \] (230)

Thus the \( \{q_j\} \) are compatible with the given data and we have also that
\[ \ln (p_j/q_j) \leq (p_j/q_j) - 1, \] (231)
with equality only if \( p_j = q_j \), taking the \( \{p_j\} \) as normed probabilities.
Multiplying this relation by $q_j$ and summing over all eigenstates gives

$$
\sum_j q_j \ln \left( \frac{p_j}{q_j} \right) \leq \sum_j q_j \left( \frac{p_j}{q_j} - 1 \right),
$$

(232)
i.e.

$$
\sum_j q_j \ln (p_j) - \sum_j q_j \ln (q_j) \leq \sum_j p_j - \sum_j q_j = 0,
$$

(233)
on making use of the probability normalisation conditions. Hence we find

$$
\sigma(\{q_j\}) = -\sum_j q_j \ln (q_j) \leq -\sum_j q_j \ln (p_j),
$$

(234)
with equality only when all $q_j = p_j$.

Now substitute Eq.(226) for the canonical $\{p_j\}$ into Eq.(234) to obtain

$$
\sigma(\{q_j\}) \leq -\sum_j q_j [-\beta E_j - \ln (Z)],
$$

(235)
which by use of the constraint equations (230) becomes

$$
\sigma(\{q_j\}) \leq \beta \bar{E} + \ln (Z) = \sigma(\{p_j\})
$$

(236)
the last equality following easily from Eqs.(219) and (226).

The basic point to observe about the relation (236) is that it applies to any arbitrary set of probabilities $\{q_j\}$ which happens to satisfy the few constraints imposed by experiment. The quantity $\beta \bar{E} + \ln [Z(\beta, V, N)]$ in Eq.(236) depends only on the given data $(\bar{E}, V, N)$ since $\beta$ is determined from that same data by Eq.(229). Hence it remains constant as the probabilities $\{q_j\}$ are varied (consistently with the data constraint equations). Therefore, for all sets $\{q_j\}$ which agree with the data, i.e., which satisfy $\sum_j q_j = 1$ and $\sum_j q_j E_j = \bar{E}$, we have

$$
\sigma(\{q_j\}) \leq \sigma(\{p_j\}) = \beta \bar{E} + \ln [Z(\beta, V, N)]
$$

(237)
We conclude that $\sigma(\{p_j\})$ is the absolute maximum of $\sigma$ under the given constraints since equality in Eq.(237) is attained only when all

$$
q_j = p_j = \frac{\exp [-\beta E_j(V, N)]}{Z(\beta, V, N)}.
$$

(238)
To finish this subsection we gather together the basic results. Under the conditions \( \sum_j p_j = 1 \) and \( \sum_j p_j E_j = \bar{E} \) the uncertainty function \( \sigma = -\sum_j p_j \ln(p_j) \) is maximised by the canonical probabilities

\[
p_j = \frac{\exp[-\beta E_j(V,N)]}{Z(\beta, V, N)},
\]

in which

\[
Z(\beta, V, N) = \sum_j \exp[-\beta E_j(V,N)],
\]

and the Lagrange multiplier \( \beta \) is related to \( \bar{E} \) by the equation

\[
\bar{E} = -\frac{\partial \ln[Z(\beta, V, N)]}{\partial \beta}.
\]

The maximised uncertainty function itself then takes the value

\[
\sigma_{\text{max}}(\{p_j\}) = \beta \bar{E} + \ln[Z(\beta, V, N)].
\]

We emphasise that these formulae apply to any system whatever that is in equilibrium under isothermal (constant \( T \)) conditions. They constitute in fact the fundamental machinery of statistical mechanics and in principle require no further development except to incorporate additional relevant macroscopic variables for specific systems. In the last subsection of this section we will extend the formalism itself in a minor way in order to ease the computational problems for quantum gases and to treat systems for which only the mean particle number is specified, but no essentially new ideas are involved.

### 5.3 Meaning of temperature

The purpose of this subsection is to explain further the significance of the parameter \( \beta \) which arises naturally in the canonical formalism. We assume throughout the principle of conservation of energy or, as it is called in thermal physics, the First Law of Thermodynamics.

We show first that the value of \( \beta \) for a given system depends only on the differences of the energy eigenvalues, and assumed mean energy, from an arbitrary reference point. This is a necessary step in the demonstration that \( \beta \) has an absolute physical significance since energy is definable only
up to an additive constant. Thus all the energy eigenvalues \( \{E_i\} \) of a particular body must be referred to a constant energy of freely chosen value \( E_0 \), and they may be written as

\[
E_j = \epsilon_j + E_0,
\]

in which only the differences \( \{\epsilon_j\} \) are physically relevant.

It follows easily from the normalisation of the eigenstate probabilities that the specified mean energy \( \bar{E} \) of the system also contains the same arbitrary constant \( E_0 \) since we have

\[
\bar{E} = \sum_j p_j E_j = \sum_j p_j (\epsilon_j + E_0) = \bar{\epsilon} + E_0,
\]

so that the physically relevant quantity is the mean energy difference

\[
\bar{\epsilon} = \sum_j p_j \epsilon_j = \sum_j p_j (E_j - E_0).
\]

The demonstration that the canonical probabilities \( \{p_j\} \) do not depend on \( E_0 \) follows simply from the Eqs.\((239)\) and \((240)\) of the previous subsection. On substituting into them Eq.\((243)\) above we find easily that the distribution no longer contains the constant \( E_0 \) explicitly, but is expressed in terms of the set of energy differences \( \{\epsilon_j\} \). At the same time, the parameter \( \beta \) is clearly determined by the relation Eq.\((245)\), just given, which involves \( \bar{\epsilon} \). This result is already a strong indication that the value of \( \beta \) can be given an absolute significance, in contrast to energy values. We will, however, retain the previous notation for energies on the understanding that the canonical formalism really depends only on energy differences. It is often convenient to take the \( \{E_j\} \) as the excitation energies of a system above its ground state and, with this convention, it is not very difficult to see what various possible extreme values for \( \beta \) might imply.

Take the ground state energy to be \( E_0 = 0 \) and suppose first that \( \beta \to \infty \). Then, since all excited states of the system have \( E_j > 0 \), \( \exp(-\beta E_j) \to 0 \); from which it follows that the corresponding \( p_j \to 0 \), while states with the ground energy retain finite equal probabilities. On the other hand, if we suppose that \( \beta \to +0 \), i.e., approaches zero from above, then all \( p_j \) clearly tend towards equality, though states with lower energies always have greater probabilities. When the system has no finite upper bound to its possible energy eigenvalues, the limiting value \( \beta = 0 \)
would not be sensible, since the state probabilities for finite energy would vanish. Hence $\beta > 0$ is the usual situation in thermal physics; but it is sometimes possible to isolate effectively, in a real body, a subsystem which does have a finite number of energy eigenstates. In this case the value $\beta = 0$ leads at once to equal non-zero probabilities for all eigenstates and it even becomes sensible to consider what happens when $\beta$ is taken to be negative. Inspection of the expression for $p_j$ now shows that the states with greater energy have larger probability and that $p_j \to 0$ as $\beta \to -\infty$, excepting only the $p_j$ for states having the maximum allowed energy eigenvalue, which become equal. To summarise, for all real bodies in complete thermal equilibrium, the physically possible values of $\beta$ lie in the range $0 < \beta \leq \infty$ while for subsystems with a maximum energy, which can also be isolated long enough to come to internal equilibrium, values of $\beta$ in the range $-\infty \leq \beta \leq 0$ may be possible in addition.

Subsystems described by negative $\beta$ are said to be inverted, since their state probabilities \{\textit{p}_j\} increase with increasing $E_j$, in sharp contrast to the situation for all bodies in complete equilibrium. We shall soon see that subsystems with $\beta \leq 0$ are always hotter than any body having positive $\beta$. However, it must be said that these negative temperature systems are of extremely specialised interest and we will touch on them only briefly in the remainder of this article. In what follows, therefore, we will restrict ourselves mainly to consideration of bodies in complete internal equilibrium among all degrees of freedom and take it that the possible values of $\beta$ are somewhere in the range $0 < \beta \leq \infty$. We are led to the adoption of strictly positive $\beta$ in the formalism by the discussion above and the observation that physical systems have no definite upper limit to their energy spectra when all their mechanical variables are taken into account. Attainment of the extreme value $\beta = \infty$ is believed to be impossible for any real body. That limit would correspond, as we saw, to the system being brought to its ground state; but this does not seem to be achievable by macroscopically feasible processes. The matter will not be discussed further here, except to note that a formal statement of such effective impossibility is very often taken as an axiom and called the Third Law of Thermodynamics.

The next step is to apply the canonical method to a system composed of two bodies, each
in complete internal equilibrium and also in a state of *mutual* equilibrium with each other. The composite body can be thought of as either isolated or in equilibrated energy contact with another, much larger body, which acts as a source or sink for heat transfer. Under the stated conditions, the composite system may be ascribed a definite mean total energy $\bar{E}$, and the component bodies will also possess well defined average energies $\bar{E}_1$ and $\bar{E}_2$, such that $\bar{E} = \bar{E}_1 + \bar{E}_2$. We assume that the interaction coupling the two bodies is sufficiently large that energy equilibrium is established easily, but at the same time is essentially negligible compared with the individual Hamiltonians. Hence to excellent approximation the total Hamiltonian $\hat{H}$ may be written in terms of the two subsystem energy operators as $\hat{H} = \hat{H}_1 + \hat{H}_2$. The Schrödinger equation for the energy eigenstates and eigenvalues of the compound body has the form

$$\hat{H}|\psi_i\rangle = (\hat{H}_1 + \hat{H}_2)|\psi_i\rangle = E_i|\psi_i\rangle,$$

and it is easy to see that the eigenstates are products of eigenstates of the individual bodies while the eigenvalues are sums of corresponding separate eigen-energies. Thus, on writing the compound state labels $(i)$ as $(i) = (jk)$, where the sets of quantum numbers $(j)$ and $(k)$ refer to the states of bodies 1 and 2, respectively, we have that

$$|\psi_i\rangle = |\varphi_j\rangle|\chi_k\rangle \quad \text{and} \quad E_i = E_j + E_k,$$

in which the states $|\varphi_j\rangle$ and $|\chi_k\rangle$ of bodies 1 and 2 are solutions of

$$\hat{H}_1|\varphi_j\rangle = E_j|\varphi_j\rangle \quad \text{and} \quad \hat{H}_2|\chi_k\rangle = E_k|\chi_k\rangle.$$  

Equilibrium probabilities $\{p_i\}$, for the occurrence of the eigenstates $|\psi_i\rangle$ of the composite body, are assigned by maximising the uncertainty

$$\sigma(\{p_i\}) = -\sum_i p_i \ln (p_i),$$

subject to the assumed constraints

$$\sum_i p_i = 1 \quad \text{and} \quad \sum_i p_i E_i = \bar{E}.$$
By the arguments of the last subsection this process leads to the result

\[ p_i = \frac{\exp(-\beta E_i)}{Z(\beta)}, \]  

(251)

where

\[ Z(\beta) = \sum_i \exp(-\beta E_i), \]  

(252)

and the parameter \( \beta \) is related to the total mean energy value by

\[ \bar{E} = -\frac{\partial \ln(Z(\beta))}{\partial \beta}. \]  

(253)

The maximised uncertainty itself is then expressed by

\[ \sigma_{\text{max}} = \beta \bar{E} + \ln[Z(\beta)]. \]  

(254)

By replacing each compound eigenvalue \( E_i \) by the corresponding sum of the eigenvalues \( E_j \) and \( E_k \), as indicated in Eq.(247), we see immediately, from the elementary properties of the exponential function, that we may write

\[ p_i = p_j p_k, \]  

(255)

with

\[ p_j = \frac{\exp(-\beta E_j)}{Z_1(\beta)} \quad \text{and} \quad p_k = \frac{\exp(-\beta E_k)}{Z_2(\beta)}, \]  

(256)

where

\[ Z_1(\beta) = \sum_j \exp(-\beta E_j) \quad \text{and} \quad Z_2(\beta) = \sum_k \exp(-\beta E_k), \]  

(257)

and the same value of \( \beta \) as above is used in the separated equations.

It is also clear from Eqs.(247), (250) and (255) that \( \bar{E} \) may be written as

\[ \bar{E} = \bar{E}_1 + \bar{E}_2, \]  

(258)

in which

\[ \bar{E}_1 = \sum_j p_j E_j \quad \text{and} \quad \bar{E}_2 = \sum_k p_k E_k. \]  

(259)

Alternatively, these relations may be derived easily from Eq.(253) since it is obvious that \( Z(\beta) = Z_1(\beta) Z_2(\beta) \). Inspection of Eqs.(256), (257) and (259) now reveals that the expressions for the
sets of numbers \( \{p_j \} \) and \( \{p_k \} \) are exactly of the form of canonical probabilities for the separate systems 1 and 2, respectively, and would in fact be numerically equal to such probabilities if the mean energies of those systems were known to have the values \( \bar{E}_1 \) and \( \bar{E}_2 \). The uncertainties associated with the bodies, separately considered, would then have the maximum values for that input information. Thus from Eq.(254) we would have for the composite body that

\[
\sigma_{\text{max}} = \beta (\bar{E}_1 + \bar{E}_2) + \ln [Z_1(\beta)Z_2(\beta)]
\]

\[
= \{ \beta \bar{E}_1 + \ln [Z_1(\beta)] \} + \{ \beta \bar{E}_2 + \ln [Z_2(\beta)] \}
\]

\[
= \sigma_{\text{max}}(1) + \sigma_{\text{max}}(2).
\]

(260)

We conclude therefore, as a consequence of our uncertainty maximisation principle, that Eqs.(256)–(259) determine the average energies \( \bar{E}_1 \) and \( \bar{E}_2 \) possessed by two bodies, in equilibrated thermal contact, which together comprise a single compound system of given mean energy \( \bar{E} \). It is clear in addition that each of the components must have the same value for its \( \beta \) parameter as is required in the description of the composite body.

Yet another way to derive this equality of \( \beta \) values is to consider small changes in the mean energies \( \bar{E}_1 \) and \( \bar{E}_2 \) consistent with the total average energy \( \bar{E} = \bar{E}_1 + \bar{E}_2 \) remaining constant. For the total uncertainty to be a maximum such variations must give

\[
\frac{\partial \sigma_{\text{max}}}{\partial \bar{E}_1} = \frac{\partial \sigma_{\text{max}}(1)}{\partial \bar{E}_1} + \frac{\partial \sigma_{\text{max}}(2)}{\partial \bar{E}_1} = 0,
\]

(261)

i.e.,

\[
\frac{\partial \sigma_{\text{max}}(1)}{\partial \bar{E}_1} = \frac{\partial \sigma_{\text{max}}(2)}{\partial \bar{E}_2}
\]

(262)

But from the general relations Eq.(241) and (242) of the last subsection we get

\[
\frac{\partial \sigma_{\text{max}}}{\partial \bar{E}} = \frac{\partial[\beta \bar{E} + \ln Z(\beta)]}{\partial \bar{E}}
\]

\[
= \beta + \left[ \bar{E} + \frac{\partial \ln Z(\beta)}{\partial \beta} \right] \frac{\partial \beta}{\partial \bar{E}}
\]

\[
= \beta.
\]

(263)

Hence, on applying this to Eq.(260), and using also Eq.(261) and (262), we find that

\[
\beta = \beta_1 = \beta_2.
\]

(264)
This shows that the uncertainty maximisation conditions for description of mutual equilibrium, mentioned at the end of subsection 4.4 are equivalent to setting the parameters $\beta$ of canonical distributions to be equal. We see, therefore, that $\beta$ has at least one of the operational characteristics of empirical temperature, namely having equal values for bodies in mutual equilibrium. For any particular system, the quantity $\beta$ may, in theory, be obtained from a knowledge of the energy excitation spectrum, the degeneracies of the quantum states and the specified mean energy. It is moreover, independent of the arbitrarily chosen reference point with respect to which the energies are reckoned. But eventually we will need to show that $\beta$ can also be determined empirically without such detailed microscopic information. The macroscopic measurement of $\beta$ will not, by itself, enable us to infer the quantal energy spectrum or even the total energy $\bar{E}$ of the system. Measurement of $\bar{E}$ requires the further techniques of calorimetry for estimating energy transfers. In practice, one of the fundamental concerns of thermal physics is the dependence of energy on temperature, since the observed relationships throw much light on the internal constitution of bodies.

It now remains to show that we can correlate the values of $\beta$ for two bodies, each initially in equilibrium, with the direction in which a spontaneous net energy transfer occurs when the bodies come into thermal contact. We assume that matters are arranged so that the bodies exchange energy only by essentially microscopic interactions occurring at the interface and not by any processes recognisable macroscopically as work. This corresponds experimentally to heat transfer.

Consider, therefore, two systems, each with a fixed volume and number of particles, one with mean energy $\bar{E}_1$, and corresponding $\beta_1$, the other with mean energy $\bar{E}_2$ and appropriate $\beta_2$, such that $\beta_1 < \beta_2$. If they are now placed in thermal contact, through a wall allowing only spontaneous transfer of heat energy, then it is a reproducible fact of observation that energy will indeed be exchanged between them, until thermal equilibrium is once again established. We assume that the volumes of the bodies are held at their initial values throughout this in general irreversible process and that the composite system is also isolated from external influences so that the total
energy stays constant at the initial value of $\bar{E}_1 + \bar{E}_2$. At the final condition of complete mutual equilibrium both bodies, and the conjoined system, may all be described by canonical distributions, over corresponding eigenstates, with the same parameter value $\beta$. The separate energies of the two bodies will now have assumed some new values $\bar{E}_1'$ and $\bar{E}_2'$ satisfying $\bar{E}_1' + \bar{E}_2' = \bar{E}_1 + \bar{E}_2$. Writing the energy transfer from the first body to the second as $\delta \bar{E}$, the final energies are represented by

$$\bar{E}_1' = \bar{E}_1 - \delta \bar{E} \quad \text{and} \quad \bar{E}_2' = \bar{E}_2 + \delta \bar{E}. \quad (265)$$

We will now demonstrate that, under the given conditions, the body with the lower initial value of $\beta$ will lose energy to the other body and that the final $\beta$ value at equilibrium will lie between the separate initial values. That is, if $\beta_1 < \beta_2$ as assumed above, then the energy transfer $\delta \bar{E} > 0$ and $\beta_1 < \beta < \beta_2$. The simple proof depends only on a consideration of the rate of change of mean energy $\bar{E}$ with $\beta$ at constant volume. If the volume and particle number of a system are maintained at fixed values, then the Hamiltonian, energy eigenstates and eigenvalues are unchanging and a variation of the mean energy $\bar{E} = \sum_j E_j p_j$ to a new equilibrium value is described entirely by altering the value of $\beta$ entering the expression for the canonical probabilities, namely, $p_j = \exp (-\beta E_j)/Z(\beta)$. Therefore,

$$\frac{\partial \bar{E}}{\partial \beta} = \sum_j E_j \frac{\partial p_j}{\partial \beta} = \sum_j E_j p_j \frac{\partial \ln (p_j)}{\partial \beta}$$

$$= - \sum_j E_j p_j \left[ E_j + \frac{\partial \ln Z(\beta)}{\partial \beta} \right]$$

$$= - \sum_j E_j (E_j - \bar{E}) p_j, \quad (266)$$

in which we have used the relation $\bar{E} = -\partial \ln Z(\beta)/\partial \beta$ derived earlier.

It is now easy to see, from the definition of $\bar{E}$ and the normalisation of the probabilities, that this result may be cast in the more useful form

$$\frac{\partial \bar{E}}{\partial \beta} = - \sum_j (E_j - \bar{E})^2 p_j = - (\Delta E)^2 \quad (267)$$

where it is plain that the $(\Delta E)^2$, the expected square deviation of the system energy from the mean, is strictly positive for all finite values of $\beta$. A further simple deduction is that $\partial \bar{E}/\partial \beta$ approaches
zero (from below) only as $\beta$ moves towards infinity, where the only surviving probabilities are those for the lowest, or highest, levels. We conclude from Eq.(267) that for all attainable $\beta$ the mean energy $\bar{E}$ at equilibrium is a strictly decreasing function of $\beta$.

Application of this result to the case of two bodies in thermal contact, as set out above, is straightforward. The final, common $\beta$ value for the systems can not be less than the smaller initial value because then both bodies would have gained energy, which is impossible if energy is to be conserved overall. Similarly, the final $\beta$ can not be bigger than the larger of the initial values; hence it must take on a value in the range $\beta_1 < \beta < \beta_2$. It follows, from the proved decrease of the expected energy with increasing $\beta$, that the first body loses energy while the second one gains an equal amount. Thus in Eq.(265) we have that the quantity $\delta\bar{E} > 0$. We may also remark that nowhere in the argument has it been necessary to assume that the values of $\beta$ be positive. A corollary of the basic result is, therefore, that a system with $\beta < 0$ is expected to lose energy when put into thermal contact with a body having $\beta > 0$. Thus systems assigned negative temperatures are hotter than all ordinary bodies possessing the usual positive temperature.

This completes our demonstration that the relative hotness of bodies may be ordered in terms of their canonical distribution parameters $\beta$. All the supporting arguments are, of course, really statistical in character since we have employed throughout the probabilistic notions of expected values of energy and of mean square deviations from the average. We have also made a quite extensive use of our theorems on the maximisation of uncertainty and the physical assumptions underlying them. To finish this subsection, we discuss how $\beta$ can be found experimentally and related to the conventional absolute temperature $T$ of thermodynamics.

In order to determine the value of $\beta$ for a body in equilibrium it should be entirely sufficient to place it in thermal contact with some suitable subsidiary body which can act as a thermometer. It is assumed of course that mutual equilibrium will soon be attained, that the presence of the thermometer does not greatly perturb the original equilibrium state of the investigated body, and that the substances used for measurement have some hotness dependent properties whose relation to the common $\beta$ value can be analysed completely. The possibility of constructing a reliable
empirical temperature scale does not in fact depend on the last proviso. All that is required for an empirical scale is that the chosen indicator properties can be reproducibly ordered, so that they can serve as easily recordable criteria for equal or relative hotness of bodies. There are many materials and instruments with properties suitable for establishing such practical measures. Examples include the length of a mercury column in a glass capillary tube, the electrical resistance of platinum and the potential difference between junctions in a closed circuit formed by two different metallic wires. Electrical devices, in particular, can be made very rapidly acting and with such small thermal capacities that their perturbing effects are almost negligible.

The drawback of most of the practical scales is that it is troublesome to calibrate them in terms of the universal standard provided by the $\beta$ parameter of the statistical treatment, or by the equivalent absolute temperature $T$ of thermodynamics. It is certainly necessary to undertake this task of calibration before any theoretical understanding of thermal behaviour can be achieved and, in low temperature physics especially, it is often forced by the absence of more direct ways for assigning the $\beta$ values. Fortunately, the subsequent development of thermodynamics shows that many properties of substances, with their corresponding empirically defined temperature scales, can be exploited experimentally to yield accurate assessment of absolute temperature. But on a rather lower level than this, there are several practical scales which have been found to possess a reasonably accurate linear relationship to absolute $T$ values. These are usually based on the easily reproducible ice and steam points of water, under one atmosphere of pressure. For a Centigrade scale these fixed points are called $0^\circ$C and $100^\circ$C, respectively, and some readily measurable property of a convenient substance is chosen to interpolate between them or to extrapolate outside the given range. A simple example is the well-known mercury in glass thermometer which is of great utility when high accuracy is not required and only a very limited variation of temperature needs to be monitored. The standard Centigrade scale can be set up by using the properties of gases. Under accessible experimental conditions it is found that all gases lead to exactly the same scale and it is this which is most nearly a linear function of the thermodynamic temperature. The absolute zero of temperature, at which all bodies reach their ground states, is then represented
approximately by the Centigrade value $-273^\circ$C. For our purposes it is not necessary to examine minutely the technical aspects of thermometry, but only to describe in sufficient detail how the gas properties alluded to above may be used to measure $\beta$ values directly. The procedure allows a useful definition of temperature requiring only one reproducible fixed point to set the numerical scale.

The main problem, as outlined above, is to establish a temperature scale which is not tied irrevocably to accidental properties of an arbitrarily chosen substance or to the quirks of a particular instrument. But at the same time the measurement method should be relatively easy to implement over a wide range of conditions. By great food fortune, Nature has given us a system which neatly fulfils all our requirements. This involves the concept of the ideal gas temperature, which proves on the one hand to be identical to the quite differently defined thermodynamic temperature and on the other hand can be found to extremely good approximation from data on real gases. The purely thermodynamic definition of temperature will be discussed later; our present interest is to indicate in a preliminary way how an analysis of the ideal gas system enables direct access to the statistical $\beta$ values. The crucial consideration from both experimental and theoretical viewpoints is that all gases, at low enough density, can be shown to obey a law which involves macroscopic observables and the $\beta$ value in a particularly simple combination. This is called the ideal gas law. For some gases, under the same condition of low density, there also exists a simple relation between $\beta$ and the energy of a given mass of the gas; but this is of only secondary importance. More thermodynamically relevant is the observation that the energies of all sufficiently dilute bodies of gas are nearly independent of volume or pressure, over fairly large ranges, and are controlled solely by the temperature, though the functional relationships may be quite complicated.

The possibility of establishing the standard gas scale depends, firstly, on the existence of reproducible equilibrium states for the systems used to provide constant temperature environments for a gas and, secondly, on two experimental observations for real gases which can be extrapolated confidently to the ideal conditions. The results are summarised in the statement that, as the
pressure of a real gas tends to zero, at constant temperature, then the internal energy and the product $PV$ of pressure and volume both become independent of $P$ and $V$. These two empirical facts are known, respectively, as Joule’s Law and Boyle’s Law. The second gives at once a way of defining an experimental temperature scale by the relation

$$PV = R\Theta,$$  \hfill (268)

in which, for a given mass of gas, $R$ is a numerical constant determined from the measurement units and the value chosen for $\Theta$ at the fixed point used as a reference temperature.

Application of the canonical formalism to a dilute gas of $N$ molecules in volume $V$ implies the ideal gas equation

$$\bar{P}V = N/\beta,$$  \hfill (269)

where $\bar{P}$ is the statistically estimated pressure, assumed equal to $P$. The same analysis also leads to Joule’s Law, but indicates that the equation of state holds independently of the internal structure of the molecules. Comparison with Eq.(268) reveals that the empirical gas scale is related to $\beta$ values by the simple formula $\Theta = N/R\beta$. In the next subsection we prove that $1/\beta$ for any system is proportional to the thermodynamic temperature $T$ of the absolute Kelvin scale, which is defined traditionally by means of Carnot cycles. We deduce that the empirical gas scales can be read as identical to the Kelvin scale by appropriate choice of units and a fixed reference state. This result can also be derived by purely thermodynamic methods starting from the perfect gas laws. Thus, anticipating slightly, we write $\Theta = T$ and set $R/N = k_B$ so that $\beta$ values for bodies may be found directly from readings of a gas thermometer by using the relations

$$\frac{\bar{P}V}{N} = k_B T = \frac{1}{\beta},$$  \hfill (270)

5.4 Measurement of uncertainty

Having now seen that the statistical $\beta$ parameter of a system is directly measurable, we are equipped to understand how the uncertainty function may be determined by experiment. Such measurements will generally yield only the value of this quantity relative to the unknown uncertainty of some arbitrary reference states, though the difficulty can be overcome to a large extent if
the starting conditions correspond to the body being near to its ground level. For many purposes, however, it does not matter that this empirical uncertainty includes an undetermined constant, since we are often interested only in its variation from state to state. From that knowledge it is possible to deduce many interrelations between the temperature and other observable properties of a system at equilibrium. The procedures required for an exploration of changes in the uncertainty are in all respects equivalent to those needed for entropy measurements, and our demonstration of this fact completes, at last, the long chain of reasoning by which the thermodynamic entropy becomes identified with the statistical uncertainty. The argument is not altogether straightforward.

In what follows we retain the notation $\beta$ for the temperature parameter, since this is traditional in the statistical theory, but keep always in mind that it is related to the ideal gas scale temperature by $\beta = 1/(k_B\Theta)$, where $k_B$ is Boltzmann’s constant. Further, it is useful at this stage to accept that $\Theta = T$, in which $T$ denotes the absolute or Kelvin temperature defined independently of particular substances, though we have not yet proved this equality. For an understanding of our current argument it is really only necessary to grasp that $\beta$ is accessible from experiments and that detailed knowledge of microstructure is not presupposed. We assume, therefore, that a system can be prepared in some reproducible reference state with definite values of volume $V$ and number of particles $N$, and with a temperature determined by the reading of a thermometer placed in close thermal contact. It is not possible to deduce the internal energy of the body from this meagre information; the numerical values of energy are anyway arbitrary unless some fixed zero point has been specified. Neither can anything be said about the underlying quantum energy levels.

It is clear that our initial knowledge about the body falls far short of enabling us to calculate the initial value of the maximised uncertainty, denoted by $\sigma_I$. The canonical formalism does however imply some definite value for this quantity and also a definite magnitude of the expected or mean energy $\bar{E}_I$, both depending on the observed temperature parameter $\beta_I$. All we can hope to learn further about the system from gross macroscopic manipulations is how the internal energy changes as the body goes from one equilibrium state to another. We assume that it is also possible
to monitor the corresponding changes in temperature, volume and pressure.

The link between processes in thermal physics and the equilibrium states central to ordinary thermodynamics lies in the idea of quasi-static and reversible change. The concept envisages the possibility of making small modifications in the surroundings of a body, and in the forces acting on it, so that the system remains effectively in equilibrium at all stages of the process. This defines the quasi-static nature of the postulated change; reversibility just means that an application of exactly the same small modifications in the opposite direction will return the system to its original condition. The sorts of change considered include addition or extraction of energy by spontaneous transfer of heat, using external reservoirs with temperatures slightly changed from that of the body, and the performance of work on or by the body, induced by alterations in the applied pressure. By such means the system can be brought by slow stages from the initial state to a final equilibrium state. The information on changes of energy, temperature and entropy, gained in this way, is vital for an understanding of the many processes which can connect equilibrium states through intermediate conditions arbitrarily far from equilibrium.

The concept of quasi-static and reversible change is, of course, only an idealisation, and in practice the process must be approximated by finite steps. We shall denote such a small, but finite, increment in a quantity $x$ by $\delta x$ and assume that the variations can be extrapolated to a limit in which it is sensible to construct experimental versions of differentials and integrals. We also need to know that changes in the internal energy of a body between two states can be found by direct measurement of work done adiabatically. This work is not itself required to be quasi-static, but it is in general possible to perform it in one direction only, since states adiabatically accessible from a given starting point can not have a smaller uncertainty. In many practical implementations of quasi-static processes the energy increments are found just from the recorded changes in temperature, using previous data on the thermal capacity of the body, i.e., the value of $\partial E/\partial \beta$, measured under appropriate constraints.

After this brief sketch of the experimental background, stripped of most technical details, we can consider how the maximised uncertainty changes between neighbouring equilibrium states.
We denote the initial value by \( \sigma_I \) and recall from Eq.(242) the maximal uncertainty formula

\[
\sigma_{\text{max}} = \beta \bar{E} + \ln [Z(\beta, V, N)], \tag{271}
\]

the numerical value of which could, in principle, be calculated from a knowledge of the microstructure and the measured \( \beta \) since the mean energy \( \bar{E} \) is determined by Eq.(241) i.e.,

\[
\bar{E} = -\frac{\partial \ln [Z(\beta, V, N)]}{\partial \beta}. \tag{272}
\]

It is also convenient to recall here the expressions for the partition function \( Z \) and the probabilities \( p_j \) (Eqs.(240) and (239)):

\[
Z(\beta, V, N) = \sum_j \exp [-\beta E_j(V, N)], \tag{273}
\]

and

\[
p_j = \frac{\exp [-\beta E_j(V, N)]}{Z(\beta, V, N)}. \tag{274}
\]

To simplify the notation we shall from now on drop the suffix (max) from the uncertainty \( \sigma \) and suppress the dependence on \( N \), assuming for present purposes that \( N \) is fixed. This restriction is easily lifted if required. We should further bear in mind that the volume \( V \), which enters into the definition of the Hamiltonian, is taken only as a representative of many such parameters that could influence the energy eigenvalues. They define, the externally controllable environment of the system and modifying them corresponds to the performance of macroscopically recognisable work.

An increment \( \delta V \) in the volume \( V \), for example, results in the energy change \( \delta E_j = (\partial E_j/\partial V)\delta V \), thus defining the effective pressure as \( P_j = -(\partial E_j/\partial V) \), and the work done \( \delta W \) on the body is related to the mean pressure \( \bar{P} \) by

\[
\delta W = \sum_j p_j \delta E_j = -\left( \sum_j p_j P_j \right) \delta V = -\bar{P} \delta V. \tag{275}
\]

The change in the maximised uncertainty of a system, as it proceeds from any equilibrium state to one near by, follows easily from Eq.(271) and, to first order in small finite quantities, is expressed by

\[
\delta \sigma = \beta \delta \bar{E} + \bar{E} \delta \beta + \delta (\ln Z)
\]
\[
\begin{align*}
\delta \sigma &= \beta [\delta \bar{E} + \bar{E} \delta \beta + \left( \frac{\partial \ln Z}{\partial \beta} \right) \delta \beta + \left( \frac{\partial \ln Z}{\partial V} \right) \delta V] \\
&= \beta \delta \bar{E} + \left( \frac{\partial \ln Z}{\partial V} \right) \delta V, \quad (276)
\end{align*}
\]
on making use of the general relation between \( \bar{E} \) and \( \ln Z \) given in Eq.(272).

Now, from Eqs.(273) and (274), we quickly find that
\[
\frac{\partial \ln Z}{\partial V} = \left( \frac{1}{Z} \right) \frac{\partial Z}{\partial V} = \beta \sum_j \left( -\frac{\partial E_j}{\partial V} \right) \exp(-\beta E_j) \frac{Z}{Z} = \beta \sum_j p_j P_j = \beta P, \quad (277)
\]
in which \( P_j(= -\partial E_j/\partial V) \) is the pressure exerted by the body when it is in the energy eigenstate \( \psi_j \). Thus from Eqs.(275), (276) and (277) we see that
\[
\delta \sigma = \beta [\delta \bar{E} + \bar{P} \delta V] = \beta [\delta \bar{E} - \delta W]. \quad (278)
\]

This important result indicates that the change in maximised uncertainty between neighbouring equilibrium states can be determined experimentally by multiplying the increase \( \delta \bar{E} \) of the internal energy, minus the work \( \delta W \) done on the system, by the temperature parameter \( \beta \) of the initial state. The difference between the observed increment of internal energy and the work done on the body by changes in an external variable like \( V \) can only be interpreted as arising from the transfer of some of the energy in the form of heat, absorbed from or given up to the surroundings.

We denote a small quantity of this transferred heat energy by \( \delta q = (\delta \bar{E} - \delta W) \) so that Eq.(278) may be rewritten more suggestively as
\[
\delta \sigma = \beta [\delta q], \quad (279)
\]
emphasising the close relation of uncertainty and heat exchanges. If now we replace \( \beta \) by \( 1/(k_B T) \) and define thermodynamic entropy \( S \) as \( k_B \sigma \), we find that Eq.(279) becomes identical in form to the usual analytical expression for entropy change derived from the Second Law of Thermodynamics, i.e.,
\[
\delta S = \frac{[\delta \bar{E} - \delta W]}{T} = \frac{\delta q}{T}. \quad (280)
\]
The entropy difference between initial and final states $I$ and $F$ can thus be measured by summing up the above small contributions $\delta S$ as calculated from observations of temperature and heat transfer taken during a quasi-static and reversible process connecting the two states. In the limit of extremely small steps the result may be written as the integral

$$S(F) - S(I) = \int_I^F \frac{dq}{T}.$$  \hspace{1cm} (281)

Our derivation of thermodynamics from statistical mechanics is complete. We have succeeded in showing that thermodynamic entropy and statistical uncertainty are essentially identical quantities; but we have also shown that entropy can be determined from macroscopic thermal measurement only up to an additive constant signifying the entropy of a reference state.

The result in Eq.(281) can be generalised so as to apply to any processes which begin and end with the body in thermal equilibrium. To do this, we imagine that the body may be coupled with a reservoir large enough to be considered as undergoing quasi-static and reversible changes as heat is transferred to or from the body of interest. When the resultant composite system is thermally isolated the processes occurring in it are adiabatic and we have proved generally that the total entropy $S_T$ can not decrease. Hence, writing $S$ and $S_R$, respectively, for the entropies of the body and reservoir, and using the additivity property $S_T = S + S_R$, we deduce that $S(F) + S_R(F) \geq S(I) + S_R(I)$. The small heat increments $\delta q$ of the body at each stage are equal in size, but opposite in sign, to those taken up by the reservoir; thus, from Eq.(281),

$$S_R(F) - S_R(I) = \int_I^F dq/T,$$

in which $T$ denotes the varying temperature of the reservoir. The final outcome is

$$S(F) - S(I) \geq \int_I^F \frac{dq}{T},$$ \hspace{1cm} (282)

which is known as the Clausius inequality.

The equality sign in Eq.(282) holds only when the body itself, as well as the reservoir supplying the heat, undergoes quasi-static and reversible changes and, in that case, the body will have a definable temperature at all stages, which must always be closely equal to the temperature of the reservoir when the two systems happen to be in thermal contact. For this very special case,
therefore, the $T$ in Eq.(282) can be interpreted as the temperature of the body and we recover
the result in Eq.(281).

If a body is taken round an arbitrary closed cycle which finishes in the initial equilibrium state,
then the total entropy change in the body is zero. When the necessary heat transfers are supplied
by a reservoir with a definite $T$ at any stage we have from Eq.(282) that

$$\oint \frac{dq}{T} \leq 0. \quad (283)$$

If, further, the body itself undergoes only quasi-static and reversible changes throughout the cycle
then $T$ is interpretable at all intermediate stages as the varying temperature of the body and
equality holds, i.e.,

$$\oint \frac{dq}{T} = 0. \quad (284)$$

A special example of this is called a Carnot cycle, in which the working substance composing
the body is taken round a closed cycle involving two reservoirs at different, fixed temperatures.
We shall now revert to using the canonical temperature parameter, $\beta$, since we wish to explain
how the concept of a Carnot cycle provides an operational definition of absolute temperature $T$,
showing directly how $\beta$ and $T$ are related independently of the properties of particular substances.

In this type of cycle a body starts from a condition of complete thermal equilibrium and
is made to undergo very specific kinds of quasi-static and reversible change before regaining its
original state. Only one way round the cycle will be described though the sequence can, of
course, be traversed in the opposite direction. The system is first allowed to take in energy $q_1$, as heat, from a reservoir with fixed temperature $\beta_1$, i.e., *isothermally*, meanwhile expanding
and possibly performing work on its surroundings. Secondly, the body is thermally isolated and
permitted to expand adiabatically, thus doing further external work, until it reaches a condition
with temperature represented by $\beta_2$, the value of which must be larger than the magnitude of
$\beta_1$. This follows because the performance of adiabatic work by the body will lead to a fall in the
internal energy $\bar{E}$ and we have already proved that $\partial \bar{E}/\partial \beta < 0$. In the next stage, the body is
compressed isothermally while losing heat energy $q_2$ to a reservoir at constant temperature $\beta_2$. 
This process continues until a point is reached from which the final leg of adiabatic compression completes the circuit.

In terms of $\beta$, the integral result of Eq.(284) takes the form

$$\int \beta dq = 0,$$  \hspace{1cm} (285)

and, since the heat transfer of energies $q_1$ to the body and $q_2$ from the body occur only at the respective constant reservoir temperatures $\beta_1$ and $\beta_2$, we deduce easily that

$$\beta_1 q_1 = \beta_2 q_2.$$  \hspace{1cm} (286)

No reference has been made here to the nature of the working substances; so, for any body executing a Carnot cycle, the ratio of heat supplied at $\beta_1$ to heat subtracted at $\beta_2$ is determined by the reciprocal ratio of the $\beta$ values and is independent of the internal structure. It was noticed by Kelvin that this independence, though derived by him in a different way, could be used to *define* a universal temperature scale. His treatment led him to write $q_1/q_2 = T_1/T_2$ where $T_1$ and $T_2$ denote the standard absolute temperatures of the two reservoirs. Hence we see from Eq.(286) that

$$\frac{q_1}{q_2} = \frac{T_1}{T_2} = \frac{\beta_2}{\beta_1},$$  \hspace{1cm} (287)

and it is clear that $\beta = 1/(k_B T)$, where $k_B$ is a constant. This operational relation for the $T$-value ratios is turned into a numerical scale by defining the temperature of the triple point of water, at which vapour, water and ice are in mutual equilibrium, to have the value 273.16 degrees Kelvin. On this scale the ice point is very close to $T = 273.15$ K. The modern Celsius scale $t$, which is almost a centigrade scale, has been defined by $t = T - T_0$; the steam point being assigned equal to $t = 100^\circ$C.

The constant, $k_B$, appearing in the relation

$$\beta = \frac{1}{k_B T},$$  \hspace{1cm} (288)

could now be found in principle from measurements with a gas thermometer using $\bar{PV} = N/\beta = Nk_B T$. In practice, there are better ways of determining the value of Boltzmann's constant $k_B$. 
which is given accurately by

\[ k_B = 1.380662 \times 10^{-23} \text{ Joules per Kelvin.} \]  (289)

It is useful at this point to summarise the somewhat intricate arguments connecting the statistical parameter \( \beta \) to the universal temperature \( T \) of thermodynamics. We first indicated that \( \beta \) could be measured directly, by use of a gas thermometer with readings extrapolated to ideal conditions. This step required a result from the statistical theory of an ideal gas, which we have not yet proved. The relation is \( \beta = 1/(k_B \Theta) \), where \( \Theta \) denotes the empirical gas scale temperature. It was then proved that \( \beta \propto 1/T \), in which \( T \) is the Kelvin temperature defined thermodynamically.

It follows, therefore, that the perfect gas temperature \( \Theta \) can be chosen identical to the Kelvin parameter \( T \), but the route to this equality has gone through the intermediary of the statistical theory. In order to confirm that the whole scheme is consistent, and to close the conceptual cycle, we should also show that \( \Theta \) can be chosen identical to \( T \) as a direct consequence of the analytical formulation of the Second Law in Eq.(280). This final step will also free the possibility of direct measurement of \( \beta \), for all types of system, from any dependence on a theoretical model of the ideal gas.

To accomplish this aim we consider the infinitesimal version of Eq.(280), namely \( dS = [d\bar{E} - dW]/T \), and use the definition of \( dW \) in Eq.(275) to write

\[ TdS = d\bar{E} + \bar{P}dV, \]  (290)

which is a general differential relation between functions of state that applies to any body whatever.

It follows that

\[ \left( \frac{\partial \bar{E}}{\partial S} \right)_V = T \quad \text{and} \quad \left( \frac{\partial \bar{E}}{\partial V} \right)_S = -\bar{P}, \]  (291)

and, from the irrelevance of order in second derivatives, we find that

\[ \left( \frac{\partial^2 \bar{E}}{\partial V \partial S} \right) = \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V, \]  (292)

a well-known Maxwell relation. Applying now the mathematical identity

\[ \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = -1, \]  (293)
valid when \( z = z(x, y) \), the second equality in Eq.(292) takes the form

\[
\left( \frac{\partial T}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial \bar{P}}{\partial S} \right)_V,
\]

(294)

and, on recalling the further differential identity symbolised by

\[
\left( \frac{\partial u}{\partial x} \right)_y \left( \frac{\partial u}{\partial x} \right)_y = \left( \frac{\partial u}{\partial x} \right)_y,
\]

(295)

which holds for functions \( u = u(x, y) \) and \( z = z(x, y) \) of two variables, we obtain from Eq.(294) another thermodynamic Maxwell relation, expressed by

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial \bar{P}}{\partial T} \right)_V.
\]

(296)

The possibility of making the gas scale identical to the Kelvin scale is a consequence of applying this result to the empirically determined gas laws of Joule and Boyle concerning, respectively, the internal energy of a quantity of gas and the product of pressure and volume. We state these laws again here for convenience: as the pressure of a gas tends to zero at constant temperature then both the energy \( \bar{E} \) and the product \( \bar{P}V \) become independent of \( \bar{P} \) and \( V \).

From Joule’s law we know that at low pressures \( (\partial \bar{E}/\partial V)_T = 0 \) and we deduce immediately from Eqs.(290) and (296) that

\[
\left( \frac{\partial \bar{E}}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - \bar{P} = T \left( \frac{\partial \bar{P}}{\partial T} \right)_V \bar{P} = 0,
\]

(297)

i.e.,

\[
\left( \frac{\partial \bar{P}}{\partial T} \right)_V = \frac{\bar{P}}{T},
\]

(298)

implying that

\[
\bar{P} = Tf(V),
\]

(299)

where \( f(V) \) is some so far undetermined function of \( V \). But from Boyle’s law we also know that, at low pressure, \( \bar{P}V = \text{constant} \) for fixed \( T \), which leads at once to \( f(V) \propto 1/V \). Thus we find \( \bar{P}V \propto T \). Since the gas scale is defined by \( \bar{P}V = R\Theta \), \( R \) being constant for a given mass of gas,
it follows that $\Theta \propto T$ and they may be made identical by choosing the same numerical values for them at a reproducible reference state, e.g., the triple point of water. We have now shown, by way of two empirical laws and the purely macroscopic concept of a Carnot cycle, that $\beta(=1/k_B T)$ may be found experimentally from the readings of a dilute gas thermometer satisfying

$$\bar{P}V = Nk_B T.$$ \hspace{1cm} (300)

The former step involving a model calculation for a perfect gas has thus been avoided, though it remains as a useful and entirely correct device for developing the theory. Its main drawback is that fairly complicated calculations are required to arrive at the simple formula $\bar{P}V = N/\beta$ given earlier. The advantage of our alternative derivation is that no specific assumptions about the microscopic constitution of the gas are invoked.

However, from the point of view of statistical mechanics, there exists a serious potential difficulty in the idea of a Carnot cycle. This problem has to do with how a quasi-static and reversible adiabatic change can be described in the statistical theory. Such processes are required for two stages of the Carnot cycle; but the difficulty arises whenever this type of adiabatic operation on a system needs to be considered. According to the account given earlier, the entropy of a body changes only when heat transfers are involved, and the formalism seems to predict unambiguously that slow adiabatic alterations conserve entropy. As can be seen clearly from Eq.(290), if the internal energy increment of the system is due only to work done on it, so that $d\bar{E} = -PdV$, then it appears to be inescapable that the change of entropy $dS$ will be zero. This is in fact correct, but is nevertheless in apparent conflict with the general statistical proof, to be given later, that almost all systems will gain entropy as a result of any kind of adiabatic process, not even excluding the special type we have called quasi-static and reversible. Failure to resolve this seeming contradiction would undermine our attempts to derive thermodynamics from statistical mechanics. We shall discuss the matter again in subsection 6.3 and prove that no paradox emerges from either discipline.
5.5 Grand canonical method

We shall now develop a simple extension of the statistical formalism in which we consider the number of particles in the system as an estimated quantity rather than as being definitely known. This modification is not of the same degree of theoretical importance as the earlier transition from actual energy to estimated energy, which led to the introduction of temperature into the probabilistic description of bodies, but is nevertheless a useful calculational device for many systems and has a direct significance for bodies in *diffusive* equilibrium with each other.

One possible way to interpret the new formalism is to admit frankly that measurements of particle number yield only a statistical estimate, most usually taken to be the mean number $\bar{N}$. We recognise that the true number $N$ may depart from $\bar{N}$, but require that the deviation be small compared to $\bar{N}$ if the experimental results are to be reproducible. Alternatively, we may assume that a body could in principle, or even in fact, be placed in diffusive contact with a much larger system (a particle bath) with which it can exchange particles. If the two bodies were in mutual equilibrium, with no net transfer of energy or particles, then the system of interest can often be taken to have a sharply defined mean particle number, $\bar{N}$, as well as a definite mean energy $\bar{E}$. In either interpretation we treat the measurable particle number as having a knowable average value $\bar{N}$.

We must now revise the probabilities for occurrence of stationary states of the system to include a dependence on the actual particle number, $N$, since specification only of $\bar{N}$ leaves open the possibility of deviations and we need a rational way of taking this into account. The final result contains a fresh statistical parameter $\mu$, called the chemical potential, bearing a somewhat similar relation to $\bar{N}$ as $\beta$ does to $\bar{E}$. Another analogy to $\beta$ arises from the fact that two bodies with equal $\mu$ retain their mean particle numbers when in diffusive contact. Hence, just as equality of $\beta$ implies no net transfer of energy between thermally coupled bodies, $\mu$ is a sort of diffusive temperature signalling the absence of a net particle transfer between two bodies having the same value of this parameter.

We assume as usual that the system Hamiltonian $\hat{H}(V,N)$ is known for any $N$ and that we can
construct the orthonormal energy eigenfunctions \( \psi_j(V,N) \) belonging to the eigenvalues \( E_j(V,N) \).

The basic problem is to assign a value for the probability \( p_{N,j} \) that the body has exactly \( N \) particles and that, given \( N \), the eigenstate \( \psi_j(V,N) \) occurs at equilibrium. The probabilities \( \{ p_{N,j} \} \) then refer to exhaustive and mutually exclusive possibilities and must therefore sum to unity. Given in addition that the mean energy and mean particle number are specified, the least committal assignment of probabilities is achieved by maximising the uncertainty function

\[
\sigma = -\sum_{N,j} p_{N,j} \ln(p_{N,j}) \tag{301}
\]

subject to the constraints

\[
\sum_{N,j} p_{N,j} = 1, \quad \sum_{N,j} p_{N,j} E_j(V,N) = \bar{E} \quad \text{and} \quad \sum_{N,j} p_{N,j} N = \bar{N}. \tag{302}
\]

We proceed by varying the probabilities \( \{ p_{N,j} \} \) and equating the induced variation of \( \sigma \) to zero. This gives

\[
-\delta \sigma = \sum_{N,j} [1 + \ln(p_{N,j})] \delta p_{N,j} = 0 \tag{303}
\]

in which the allowed increments \( \{ \delta p_{N,j} \} \) are constrained by

\[
\sum_{N,j} \delta p_{N,j} = 0, \quad \sum_{N,j} \delta p_{N,j} E_j(N,V) = 0 \quad \text{and} \quad \sum_{N,j} \delta p_{N,j} N = 0. \tag{304}
\]

Multiplying these restriction equations, respectively, by \( \alpha \), \( \beta \) and \( \gamma \) and adding them to Eq.(303) then gives

\[
\sum_{N,j} [\alpha + 1 + \beta E_j(V,N) + \gamma N + \ln(p_{N,j})] \delta p_{N,j} = 0, \tag{305}
\]

which, by the now familiar argument, may be satisfied by setting all the bracketed coefficients of the \( \delta p_{N,j} \) to zero. Thus, for all \((N,j)\),

\[
p_{N,j} = \exp(-\alpha - 1) \exp(-\beta E_j(V,N) - \gamma N). \tag{306}
\]

The factor \( \exp(-\alpha - 1) \) is easily eliminated by use of the first constraint of Eq.(302). The result for the maximising probabilities then appears in the clearly normalised form

\[
p_{N,j} = \frac{\exp(-\beta E_j(V,N) - \gamma N)}{\Xi(\beta,\gamma,V)}, \tag{307}
\]
where
\[ \Xi(\beta, \gamma, V) = \sum_{N,j} \exp \left( -\beta E_j(V, N) - \gamma N \right). \] (308)
The other constraints on the \( \{p_{N,j}\} \) lead to implicit equations for \( \beta \) and \( \gamma \) in terms of the presumed data \( \bar{E} \) and \( \bar{N} \). Substitution of Eqs.(307) and (308) into the second and third of Eqs.(302), followed by obvious manipulations, soon shows that
\[ E = -\frac{\partial \ln [\Xi(\beta, \gamma, V)]}{\partial \beta} \] (309)
and
\[ \bar{N} = -\frac{\partial \ln [\Xi(\beta, \gamma, V)]}{\partial \gamma} \] (310)
We also record, for completeness, that the mean pressure is given by
\[ \beta \bar{P} = \frac{\partial \ln [\Xi(\beta, \gamma, V)]}{\partial V}. \] (311)
This is derived using the result that \( P_j = -\partial E_j(V, N)/\partial V \) in state \( \psi_j(V, N) \).

The value of the maximised uncertainty is found by inserting Eq.(307) into Eq.(301) and making use of Eq.(302) once more. This gives
\[ \sigma_{\text{max}} = -\sum_{N,j} p_{N,j} \ln (p_{N,j}) \]
\[ = -\sum_{N,j} p_{N,j} \left\{ -\beta E_j(V, N) - \gamma N - \ln [\Xi(\beta, \gamma, V)] \right\} \]
\[ = \beta \bar{E} + \gamma \bar{N} + \ln [\Xi(\beta, \gamma, V)]. \] (312)
The proof that this is the \textit{absolute} maximum of the uncertainty function, under the given constraints, follows the same lines as given for the canonical uncertainty. We still need, however, to establish the physical significance of the grand canonical parameters \( \beta \) and \( \gamma \). This is most easily done by a minor extension of the arguments of the last two subsections. As anticipated by the notation, the new \( \beta \) is just the same directly accessible temperature parameter that we found before. The extra statistical parameter \( \gamma \) determines, by its values, whether any particle transfer occurs between diffusively coupled bodies. We start by considering how \( \sigma_{\text{max}} \) changes as the input data \( \bar{E} \) and \( \bar{N} \) are varied.
On differentiating Eq.(312) with respect to $\bar{E}$, we obtain

$$
\left( \frac{\partial \sigma_{\text{max}}}{\partial \bar{E}} \right)_{\bar{N},V} = \beta + \bar{E} \left( \frac{\partial \beta}{\partial \bar{E}} \right) + \bar{N} \left( \frac{\partial \gamma}{\partial \bar{E}} \right) + \left( \frac{\partial \ln \Xi}{\partial \beta} \right) \left( \frac{\partial \beta}{\partial \bar{E}} \right) + \left( \frac{\partial \ln \Xi}{\partial \gamma} \right) \left( \frac{\partial \gamma}{\partial \bar{E}} \right),
$$

(313)

which, on using Eqs.(309) and (310), becomes

$$
\left( \frac{\partial \sigma_{\text{max}}}{\partial \bar{E}} \right)_{\bar{N},V} = \beta.
$$

(314)

By a similar process we also derive easily that

$$
\left( \frac{\partial \sigma_{\text{max}}}{\partial \bar{N}} \right)_{\bar{E},V} = \gamma.
$$

(315)

Now apply these results to two bodies, labelled 1 and 2, each separately in equilibrium, which remain equilibrated if placed in close contact and permitted to exchange both energy and particles. If the composite system is assumed to be isolated then the total energy $\bar{E}$ and particle number $\bar{N}$ are constant and we have, from

$$
\bar{E} = \bar{E}_1 + \bar{E}_2 \quad \text{and} \quad \bar{N} = \bar{N}_1 + \bar{N}_2,
$$

(316)

that changes in the respective quantities must satisfy

$$
\delta \bar{E}_1 + \delta \bar{E}_2 = 0 \quad \text{and} \quad \delta \bar{N}_1 + \delta \bar{N}_2 = 0.
$$

(317)

The total uncertainty at complete equilibrium should be given by

$$
\sigma_{\text{max}} = \sigma_{\text{max}}(1) + \sigma_{\text{max}}(2),
$$

(318)

but this can only be a maximised uncertainty if small variations of the energies and particle numbers, consistent with Eqs.(317), imply no change in $\sigma$ to first order of small quantities. Hence, using Eqs.(317), we find

$$
\left( \frac{\partial \sigma_{\text{max}}}{\partial \bar{E}_1} \right) = \left( \frac{\partial \sigma_{\text{max}}(1)}{\partial \bar{E}_1} \right) + \left( \frac{\partial \sigma_{\text{max}}(2)}{\partial \bar{E}_1} \right) = \left( \frac{\partial \sigma_{\text{max}}(1)}{\partial \bar{E}_1} \right) - \left( \frac{\partial \sigma_{\text{max}}(2)}{\partial \bar{E}_2} \right) = 0.
$$

(319)

From this last equality, and the similar one involving $\bar{N}_1$ and $\bar{N}_2$, we see that Eqs.(314) and (315) lead to the equilibrium relations

$$
\beta_1 = \beta_2 \quad \text{and} \quad \gamma_1 = \gamma_2,
$$

(320)
Thus the equality of $\beta$-values implies there is no net transfer of energy between the two bodies, while $\gamma_1 = \gamma_2$ signals the absence of systematic particle transfers. If the composite body is confined to a fixed volume, as well as being otherwise isolated, and the subsystems are permitted to do work on each other, then a consideration of small changes in $V_1$ and $V_2$, taken in conjunction with Eq.(311), proves that the state of complete equilibrium will be attained only when $\bar{P}_1 = \bar{P}_2$ also.

Here, we will not consider any further the physics of particle transfer between bodies which have different initial values of $\gamma$. We shall regard the grand canonical method merely as a very useful tool to be applied as necessary to bodies with definite particle number $N$. In general, we can only estimate the true number, but it is often quite sensible to replace this imperfectly known quantity by an average value $\bar{N}$, or the equivalent statistical parameter $\gamma$. In any particular application of the method, of course, we will need to check that the expected deviations from the mean are small compared with $\bar{N}$. We will also occasionally want to investigate the effect on the properties of a single system of changes in the number of particles estimated to be in it.

Subsequent steps in the identification of $\beta$ exactly parallel the earlier arguments given in connection with the canonical method and it would be tedious to repeat them. The result is of course that $\beta = 1/(k_B T)$, as before. The extra parameter is usually written in the form $\gamma = -\mu \beta$ and, with this replacement, the probability of finding $N$ particles in state $\psi_j(V,N)$ is

$$p_{N,j} = \frac{\exp[-\beta(E_j(V,N) - \mu N)]}{\Xi(\beta, \mu, V)}, \quad (321)$$

where

$$\Xi(\beta, \mu, V) = \sum_{N,j} \exp[-\beta(E_j(V,N) - \mu N)]. \quad (322)$$

The corresponding maximised uncertainty then takes the form

$$\sigma_{\text{max}} = \beta(\bar{E} - \mu \bar{N}) + \ln[\Xi(\beta, \mu, V)]. \quad (323)$$
6 Temperature and statistical physics

6.1 Thermodynamic potentials

Now that the machinery of statistical mechanics has been assembled, and its parallels with thermodynamics firmly established, it is useful to summarise and extend the relationships between the two theories. In this subsection, therefore, we will write down and discuss the equations which connect statistically calculable quantities to some of the most useful functions of thermodynamics. The functions alluded to are often called potentials since many of the physically significant properties of bodies can be found from them by differentiation.

As stated before, a pleasing feature of statistical mechanics is that parameters introduced for mathematical convenience turn out to have direct experimental meaning in thermal physics. In particular, the quantities arising in the three different approaches we have developed, namely, the microcanonical, canonical and grand canonical methods, are expressed automatically in terms of variables which are natural ones for the associated thermodynamic functions. A potential function is said to be expressed in its natural variables when these are such as to enable the maximum amount of thermodynamic information to be extracted from it. Knowledge of any one of the naturally expressed functions we discuss is then sufficient for construction of the others. In what follows we shall present equations relating the macroscopic and experimentally accessible functions of state to quantities derived by probabilistic methods from the known microscopic structure and given equilibrium data. We will drop arbitrary additive constants associated with the experimental starting configurations since our central concern will be to study differential properties of potentials. The initial state constants become important only when absolute values of the statistically calculated entropy are in question and not just its variation from state to state. This involves delicate, and still controversial, discussion of the status of the Third Law and its implications in low temperature physics, an extensive topic which is largely beyond our scope.

For our first example of the physical interpretation of the statistical theory we recall the microcanonical probability method, as applied to a simple homogeneous body which is adiabatically isolated and observed to be in thermal equilibrium. The body is taken to have volume $V$, ...
particle number $N$ and an estimated energy $\bar{E}$ whose value is assumed to be confined within a prescribed small energy interval, i.e., such that $E \leq \bar{E} \leq E + \Delta E$. For fixed $\Delta E$ the number of accessible energy eigenstates is a calculable function, $\Omega(\bar{E}, V, N)$, of the given data, provided that the Hamiltonian is known and that the stationary state Schrödinger equation can be solved. We showed in subsection 5.1 that under these conditions the maximised uncertainty is given by $\sigma_{\text{max}} = \ln [\Omega(\bar{E}, V, N)]$ and we further made a case for the proposition that the absolute thermodynamic entropy is numerically equal to $k_B \sigma_{\text{max}}$, where $k_B$ is Boltzmann’s constant. Hence we find that the macroscopic function called entropy appears in the form

$$S(\bar{E}, V, N) = k_B \ln [\Omega(\bar{E}, V, N)].$$

(324)

Now the fundamental equation governing small changes, whether reversible or not, in the equilibrium state of a thermodynamic system is written as

$$\delta \bar{E} = T \delta S - \bar{P} \delta V + \mu \delta N,$$

(325)

where $\delta \bar{E}$ is the increase in the internal energy and, in the reversible case, $T \delta S$ denotes the heat added, $-\bar{P} \delta V$ is the work done on the body and $\mu \delta N$ indicates the energy increment brought about by a small increase in the number of particles. The last term generalises the equation we gave before so that bodies of varying $N$ can be considered. The temperature $T$, the pressure $\bar{P}$ and the chemical potential $\mu$ are variables which have the same values throughout a body in complete equilibrium and are called intensive, as is also the particle number density of the system. In contrast, the energy $\bar{E}$, volume $V$ and entropy $S$ are additive over subdivisions of the body and can be assumed proportional to the size of the body as measured by the value of $N$. Such quantities are called extensive variables. We observe in passing that we have here made a tacit choice of the arbitrary zero of energy as that of an empty cavity which would exactly enclose the given system.

A simple rearrangement of Eq.(325) gives

$$\delta S = \frac{\delta \bar{E}}{T} + \frac{\bar{P} \delta V}{T} - \frac{\mu \delta N}{T},$$

(326)
and hence we may calculate the intensive parameters from $S$ as follows,

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{\bar{P}}{T} \quad \text{and} \quad \frac{\partial S}{\partial N} = -\mu. \tag{327}$$

Thus we see that the theoretical formula for $S$ provided by statistical mechanics, displayed in Eq.(324), is already expressed in just the right, or natural, variables for deriving other quantities of interest.

The intensive variables $T$, $\bar{P}$ and $\mu$ were introduced in our development of the statistical theory, but it is useful at this point to discuss their significance again from the viewpoint of pure thermodynamics. Although derived here in connection with the description of an isolated system at equilibrium, their full physical import emerges only when we ask whether two such bodies will remain in equilibrium when they are placed in loose contact and are free to exchange energy, volume and particles. Envisage, then, that the two bodies, labelled 1 and 2, are brought together inside a rigid box with adiabatic and impermeable walls which exactly enclose them, so that they form an isolated composite supersystem. If they are not initially in equilibrium with each other, then by the Second Law of Thermodynamics their individual energies, volumes and particle numbers will change until a mutual equilibrium is reached, at which the total entropy will be a maximum and will be the sum of the separate entropies, i.e.,

$$S(\bar{E}, V, N) = S_1(\bar{E}_1, V_1, N_1) + S_2(\bar{E}_2, V_2, N_2). \tag{328}$$

The given condition of isolation also implies the conservation equations

$$\bar{E} = \bar{E}_1 + \bar{E}_2, \quad V = V_1 + V_2, \quad \text{and} \quad N = N_1 + N_2. \tag{329}$$

The thermodynamic requirement of maximised total entropy means that any imagined (or virtual) small changes in $(\bar{E}_1, V_1, N_1)$ or $(\bar{E}_2, V_2, N_2)$ will, to first order, give zero change in $S$. Since, therefore, Eqs.(329) imply that

$$\delta \bar{E}_1 + \delta \bar{E}_2 = 0, \quad \delta V_1 + \delta V_2 = 0, \quad \text{and} \quad \delta N_1 + \delta N_2 = 0, \tag{330}$$

we find easily that

$$\frac{\partial S}{\partial \bar{E}_1} = \frac{\partial S_1}{\partial \bar{E}_1} - \frac{\partial S_2}{\partial \bar{E}_2} = 0, \tag{331}$$
\[
\frac{\partial S}{\partial V_1} - \frac{\partial S_1}{\partial V_2} = 0, \tag{332}
\]

and

\[
\frac{\partial S}{\partial N_1} - \frac{\partial S_1}{\partial N_2} = 0. \tag{333}
\]

Reference to Eqs.(327) now shows that the conditions for complete thermal, mechanical and diffusive equilibrium are given by

\[
T_1 = T_2, \quad \bar{P}_1 = \bar{P}_2 \quad \text{and} \quad \mu_1 = \mu_2. \tag{334}
\]

Hence the intensive variables are indicators of various types of mutual equilibrium between systems. Further discussion, along the lines given earlier for the temperature, points to the possibility of ordering their values so as to be able to predict the direction of spontaneous change when bodies with different values of the intensive parameters are placed in contact. The final result is of course that if \( T_1 > T_2 \) then the first system loses energy, if \( \bar{P}_1 > \bar{P}_2 \) it loses volume and if \( \mu_1 > \mu_2 \), it loses particles.

The entropy maximisation principle can also be applied to derive some useful conclusions about a single homogeneous isolated body, regarded as made up of a large number of small subsystems in mutually equilibrated contact with each other. Each subregion can be thought of as having its own entropy, energy, volume and particle number which add up to give the total \( S, \bar{E}, V \) and \( N \) of the isolated body. By arguments similar to those given above, it is easy to see that at complete mutual equilibrium the temperature, pressure and chemical potential will be uniform throughout the body. Furthermore, from the additivity of the extensive quantities, it is clear that if the body is augmented in size by a factor \( \lambda \), keeping all the intensive parameters constant, then we can deduce at once that

\[
S(\lambda \bar{E}, \lambda V, \lambda N) = \lambda S(\bar{E}, V, N), \tag{335}
\]

i.e., that \( S \) is a homogeneous function of order unity in its variables.

Applying Euler’s theorem on such functions we have that

\[
\bar{E} \left( \frac{\partial S}{\partial \bar{E}} \right) + V \left( \frac{\partial S}{\partial V} \right) + N \left( \frac{\partial S}{\partial N} \right) = S, \tag{336}
\]
which, on reference to Eqs.(327), yields easily that

$$\bar{E} = TS - \bar{PV} + \mu N.$$  \hspace{1cm} (337)

This result is useful in connection with the grand canonical method and its associated potential function, which will be derived later.

We expect generally that once the entropy of a system has been measured, or calculated, as a function of $(\bar{E}, V, N)$, then many other properties and relations can be deduced confidently from the thermodynamical formalism. However, the microcanonical method is only of somewhat limited interest, for two reasons. One is that measurements are more usually made of the temperature rather than the energy. The other is that it is very hard to calculate accurately the number, $\Omega$, of accessible states, even in simple models, since it is difficult to handle the constraint of fixed energy. The canonical method is almost always easier because the definite energy condition is replaced by knowledge of the simply measurable temperature, which still corresponds to a sharply defined mean energy $\bar{E}$. Fortunately, both methods, as well as the grand canonical treatment, when they can all be carried to a conclusion, give essentially identical answers for the properties of a macroscopic system. The reason is that nearly all the quantities calculated as averages turn out to have extremely small expected deviations from their means.

We come now to the canonical formalism, in which the given equilibrium data include the temperature $T$, the volume $V$ and the particle number $N$. Again, it is necessary for performing the statistical calculations that we know also the Hamiltonian of the system and its energy spectrum. From this information, the canonical method assigns probabilities for finding the energy eigenstates $|\psi_j\rangle$, belonging to energies $E_j$, in the form

$$p_j = \frac{\exp[-E_j(V,N)/k_B T]}{Z(T,V,N)},$$  \hspace{1cm} (338)

where

$$Z(T,V,N) = \sum_j \exp[-E_j(V,N)/k_B T].$$  \hspace{1cm} (339)

The maximised uncertainty is given by $\sigma_{\text{max}} = -\sum_j p_j \ln p_j$, and substitution of Eqs.(338) and
(339) into this expression soon yields, using \( \bar{E} = \sum_j p_j E_j \),

\[
k_B \sigma_{\text{max}} = S = \frac{\bar{E}}{T} + k_B \ln [Z(T, V, N)].
\]  

(340)

This suggests the definition of a new thermodynamic potential given by

\[
F(T, V, N) = \bar{E} - TS = -k_B T \ln [Z(T, V, N)].
\]  

(341)

The new function is called the Helmholtz Free Energy and we see that the canonical formalism provides a theoretical expression for it in terms of \((T, V, N)\). But these are precisely the natural variables for extracting the maximum amount of information on the thermodynamic properties of the system. To see this, consider small changes in \( F = \bar{E} - TS \) to a nearby state, i.e.,

\[
\delta F = \delta \bar{E} - T \delta S - S \delta T,
\]  

(342)

and compare this result with the fundamental thermodynamic equation

\[
\delta \bar{E} = T \delta S - \bar{P} \delta V + \mu \delta N.
\]  

(343)

Adding Eqs.(342) and (343) gives at once that

\[
\delta F = -S \delta T - \bar{P} \delta V + \mu \delta N,
\]  

(344)

which implies the differential relations

\[
\frac{\partial F}{\partial T} = -S, \quad \frac{\partial F}{\partial V} = -\bar{P}, \quad \text{and} \quad \frac{\partial F}{\partial N} = \mu.
\]  

(345)

Hence, from a knowledge of \( F \) and its natural derivatives, all quantities of interest can be inferred.

For example, since both \( F \) and \( T \) are assumed known, and \( S \) can be found by differentiation, the value of the energy \( \bar{E} \) follows from the definition in Eq.(341). The above demonstration also shows, incidentally, that the results of the statistical treatment are completely summarised by presenting the partition function, \( Z(T, V, N) \), and it is this function which is central to later developments.

The second of the Eqs.(345) is the thermodynamical version of the Equation of State of the system, that is, a relation between \( \bar{P}, V, T \) and \( N \). Putting \( F = -k_B T \ln [Z(T, V, N)] \) into that equation we get

\[
\bar{P} = k_B T \frac{\partial \ln [Z(T, V, N)]}{\partial V},
\]  

(346)
which shows how the equation of state arises in statistical mechanics. This derivation is, however, based partially on thermodynamics, so it is of some interest to demonstrate that the same equation also emerges more directly from the probability formulation. To do this, we recall that \( \bar{P} \), the average pressure, is calculated from the pressures \( P_j \) implied by the individual energy eigenstates by means of the formula

\[
\bar{P} = \sum_j P_j p_j = \sum_j \left( \frac{-\partial E_j}{\partial V} \right) p_j.
\] (347)

Substituting for \( p_j \) from Eq.(338) we find

\[
P = \sum_j \left( \frac{-\partial E_j}{\partial V} \right) \exp \left[ \frac{-E_j}{k_B T} \right] \frac{Z}{Z} \]

and an easy manipulation then gives

\[
\bar{P} = k_B T \frac{\partial}{\partial V} \ln \left[ Z(T,V,N) \right].
\] (349)

But \( \sum_j \exp \left[ -E_j/k_B T \right] = Z \), so we finally obtain the result

\[
\bar{P} = k_B T \frac{\partial}{\partial V} \ln \left[ Z(T,V,N) \right],
\] (350)
in agreement with Eq.(346).

This is further confirmation of the general consistency between thermodynamics and statistical mechanics, under the assumption that physically measurable quantities should be identified with statistical averages. It is indeed frequently easier to use the statistical method to explore the connections between experimental observables than to embark on the often esoteric manipulations required by a purely thermodynamic approach. Even for those cases in which mathematical difficulties prevent evaluation of the sums (the great majority), it is still possible to gain insight.

To conclude this subsection we discuss the grand canonical method and its associated thermodynamic potential. The assumed data are now considered to comprise the temperature \( T \), equivalent to a definite mean energy for the system, the volume \( V \) and the chemical potential \( \mu \), which implies a sharp estimated value of \( \bar{N} \) for the number of particles in the body. The macroscopic parameters \( T, V \) and \( \mu \) appear explicitly in the eigenstate probability distribution, which
is expressed by

\[ p_{N,j} = \frac{\exp\left[-(E_j(V,N) - \mu N)/k_B T\right]}{\Xi(T,\mu,V)}, \]  

(351)

where

\[ \Xi(T,\mu,V) = \sum_{N,j} \exp\left[-(E_j(V,N) - \mu N)/k_B T\right], \]  

(352)

in which the \( E_j(V,N) \) are the energy eigenvalues of a system with volume \( V \) and definite particle number \( N \). The maximised uncertainty is now given by \( \sigma_{\text{max}} = -\sum_{N,j} p_{N,j} \ln p_{N,j} \) and on using Eqs.(351) and (352) together with

\[ S = k_B \sigma_{\text{max}}, \quad \bar{E} = \sum_{N,j} p_{N,j} E_j(V,N) \quad \text{and} \quad \bar{N} = \sum_{N,j} p_{N,j} N, \]  

(353)

we quickly arrive at the result

\[ S = \frac{\bar{E}}{T} - \frac{\mu \bar{N}}{T} + k_B \ln[\Xi(T,\mu,V)]. \]  

(354)

If we now define a grand potential function by

\[ \Omega_G = \bar{E} - TS - \mu \bar{N}, \]  

(355)

then Eq.(354) shows that \( \Omega_G \) is related to the grand partition function by

\[ \Omega_G(T,\mu,V) = -k_B T \ln[\Xi(T,\mu,V)]. \]  

(356)

Yet again, the statistical method has led to a theoretical formula for a potential function and, as we shall show, expressed it automatically in its natural variables. It is also interesting that the given data and the assumed information on the microscopic structure are all subsumed in the grand partition function, which once more highlights the importance of the probability normalisation factors.

Addition of the differential version of Eq.(355), namely

\[ \delta \Omega_G = \delta \bar{E} - T \delta S - S \delta T - \mu \delta \bar{N} - \bar{N} \delta \mu, \]  

(357)

to the fundamental equation of thermodynamics,

\[ \delta \bar{E} = T \delta S - \bar{P} \delta V + \mu \delta N. \]  

(358)
gives
\[ \delta \Omega_G = -S \delta T - P \delta V - N \delta \mu, \]  
\hspace{1cm} (359)
from which it follows that
\[ \frac{\partial \Omega_G}{\partial T} = -S, \quad \frac{\partial \Omega_G}{\partial V} = -P \quad \text{and} \quad \frac{\partial \Omega_G}{\partial \mu} = -N. \]  
\hspace{1cm} (360)
Hence all quantities of thermodynamic interest are available when \( \Omega_G \), or equivalently \( \Xi \), is known as a function of \( T, \mu \) and \( V \). Again, the results have been derived in part by use of thermodynamics, so it is reassuring that, for example, the second and third of Eqs.(360), with \( \Omega_G \) replaced by \(-k_B T \ln \Xi\), can also be constructed directly from the probability functions given above in Eqs.(351) and (352).

The grand potential \( \Omega_G \) is a relatively little known thermodynamic state function, but it can be expressed in terms of more familiar quantities. This follows from the definition given in Eq.(355) and the general result given in Eq.(337). Adding those two equations shows immediately that
\[ \Omega_G = -\bar{P}V, \]  
\hspace{1cm} (361)
and so, from Eq.(356), we deduce that
\[ \bar{P}V = k_B T \ln [\Xi(T, \mu, V)], \]  
\hspace{1cm} (362)
an equation of obvious utility in the theory of gases.

### 6.2 Partition functions

In the last subsection we saw that all thermodynamical deductions from the structure information used in the canonical and grand canonical methods involved only a knowledge of the respective partition functions \( Z(T, V, N) \) and \( \Xi(T, V, \mu) \). Since these apparently trivial probability normalisation factors actually embody all the relevant microscopic details, it is useful to discuss their general properties. Also of interest is the way they are related to the accessible state number \( \Omega \) (another probability normalisation factor) and to each other. We consider this aspect first.
We begin by exhibiting once more the characteristic bridging expressions that connect thermodynamics and statistical theory. The standard methods known as (i) the Microcanonical, (ii) the Canonical and (iii) the Grand canonical formalisms lead logically to the propositions that

\begin{itemize}
  \item (i) \( S(\bar{E}, V, N) = k_B \ln [\Omega(\bar{E}, V, N)] \),
  \item (ii) \( F(T, V, N) = -k_B T \ln [Z(T, V, N)] \),
  \item (iii) \( \Omega_G(T, V, \mu) = -k_B T \ln [\Xi(T, V, \mu)] \),
\end{itemize}

with the entropy \( S \), the free energy \( F \), and grand potential \( \Omega_G \), all being expressed in their natural thermodynamic state variables.

The function \( \Omega(\bar{E}, V, N) \) represents, for an isolated system, the number of accessible energy eigenstates with energies in a small fixed interval \( \Delta E \) surrounding the estimated total energy \( \bar{E} \). The canonical method nominally refers to a body in equilibrium with a heat reservoir at temperature \( T \), so that all energy eigenstates are theoretically possible, but for which a sharply defined average energy exists, also denoted by \( \bar{E} \). The quantity at the centre of interest is now

\[ Z(T, V, N) = \sum_j \exp \left[ -\frac{E_j(V, N)}{k_B T} \right]. \tag{363} \]

This is related to the concept of accessible state number as follows. We think of the energy variable as being dissected into intervals, each one labelled by the energy \( \bar{E}_k \) at its centre. If the interval \( \Delta \bar{E}_k \), around \( \bar{E}_k \), is taken small enough, then all the energy eigenvalues in that range can be regarded as having the value \( \bar{E}_k \) and the number of such states written as \( \Omega(\bar{E}_k, V, N) \). In other words, all the eigenstates with energies falling in the interval \( \Delta \bar{E}_k \) are looked on as being effectively degenerate, with degeneracy \( \Omega(\bar{E}_k, V, N) \). The canonical partition function then appears as

\[ Z(T, V, N) = \sum_k \Omega(\bar{E}_k, V, N) \exp \left[ -\frac{E_k(V, N)}{k_B T} \right]. \tag{364} \]

It seems from this that the calculation of \( Z \) is much more difficult than evaluation of just the single degeneracy factor called for in the microcanonical method, since we now need to find the \( \Omega(\bar{E}_k) \) numbers for many energies and also perform the indicated sum for fixed particle number \( N \).
The mathematical difficulties seem to be even further increased in the grand canonical theory. Reference to Eq.(352) of the last subsection and to Eq.(363) above shows that the grand partition function can be rewritten in terms of the canonical functions \( Z(T, V, N) \), i.e.,

\[
\Xi(T, V, \mu) = \sum_N \exp \left( \frac{\mu N}{k_B T} \right) Z(T, V, N)
\]  

(365)

Hence we need to calculate \( Z(T, V, N) \) for all values of \( N \) and then perform the sum in Eq.(365). So it is difficult to believe at first sight that for many models in statistical physics the calculations actually become much easier as we go from \( \Omega \rightarrow Z \rightarrow \Xi \), since each successive stage requires all that went before and more summations. The calculations would indeed be considerably harder if they had to be done in that way. The constraints of fixed \( \bar{E} \) and \( N \) are analytically inconvenient to maintain, but we see that in the canonical theories the conditions are progressively relaxed, being replaced by assignment of the physically significant parameters \( T \) and \( \mu \). The summations representing \( Z \) and \( \Xi \) can then often be rearranged from the groupings displayed in Eqs.(364) and (365), so that the resulting unrestricted sums over all \( E_j \) and all \( N \) become much more tractable and, in some cases, can be performed exactly.

Another useful remark concerns the factorisation properties of our basic expressions. Consider first two bodies, labelled 1 and 2, in a state of mutual equilibrium mediated through surfaces allowing thermal and possibly diffusive exchange. Observation establishes the existence of a well-defined energy \( \bar{E} \) and a definite entropy \( S \) for the combined system. On separation, the two bodies are found to have individually observable energies and entropies \((\bar{E}_1, S_1)\) and \((\bar{E}_2, S_2)\) which, to good approximation, satisfy \( \bar{E} = \bar{E}_1 + \bar{E}_2 \) and \( S = S_1 + S_2 \). The question now arises as to how these facts are reflected in the formalism. If the couplings responsible for the attainment of mutual equilibrium are only small perturbations on the separate Hamiltonians, then the energy eigenvalues of the composite body are the sums of the energies of the two subsystems and the total eigenstates are products, i.e.,

\[
E_{j,k} = E_j(1) + E_k(2)
\]

(366)
and
\[ |x_{j,k}⟩ = |ψ_j⟩|ϕ_k⟩. \tag{367} \]

Using the microcanonical method, we have \( \Omega(\bar{E}_1) \) and \( \Omega(\bar{E}_2) \) as the numbers of accessible states of the two bodies in intervals \( \Delta E_1, \Delta E_2 \) near \( \bar{E}_1 \) and \( \bar{E}_2 \). Consequently, since any accessible state of the first body may occur with any accessible state of the second one, there are \( \Omega(\bar{E}) = \Omega(\bar{E}_1)\Omega(\bar{E}_2) \) states accessible to the combined system in the interval \( \Delta E = \Delta E_1 + \Delta E_2 \) near \( \bar{E} = \bar{E}_1 + \bar{E}_2 \).

We deduce that the total entropy \( S \) is given by
\[
S = k_B \ln [\Omega] = k_B \ln [\Omega_1\Omega_2] \\
= k_B \ln [\Omega_1] + k_B \ln [\Omega_2] \\
= S_1 + S_2 \tag{368}
\]

Thus the additivity of entropy follows from the factorisation properties of the accessible state numbers. The additivity of energies, of course, is an immediate consequence of Eq.(366), connecting the energy eigenvalues of the combined and individual bodies in the corresponding small energy intervals near \( \bar{E}, \bar{E}_1 \) and \( \bar{E}_2 \). All this arises naturally from the assumed smallness of the interactions responsible for equilibrium, compared with the bulk energies of the bodies.

The canonical method also implies a correspondence between thermodynamic additivity and statistical factorisation. With the same assumptions and notations as above, we now regard an observable energy as a well-defined average over all states and recall that bodies in mutual equilibrium are assigned the same temperature \( T \). Writing \( \beta = 1/k_B T \), the canonical method leads to a partition function for the composite system in the form
\[
Z(T) = \sum_{j,k} \exp \left[ -\beta \{ E_j(1) + E_k(2) \} \right] \\
= \sum_j \exp \left[ -\beta E_j(1) \right] \sum_k \exp \left[ -\beta E_k(2) \right] \\
= Z_1(T)Z_2(T). \tag{369}
\]

Since the total energy \( \bar{E}_1 \) and free energy \( F \), are given by
\[
\bar{E} = -\frac{\partial \ln [Z]}{\partial \beta} \tag{370}
\]
and

\[ F = -k_B T \ln [Z] \]  \quad (371)

we have easily that

\[ \bar{E} = \bar{E}_1 + \bar{E}_2 \]  \quad (372)

and

\[ F = F_1 + F_2. \]  \quad (373)

Also, from the definition \( F = \bar{E} - T S \), and the fact that the systems have the same temperature \( T \), we can clearly conclude that

\[ S = S_1 + S_2. \]  \quad (374)

It is equally straightforward to demonstrate the factorisability of the grand partition function under the given conditions and hence to derive the additivity of the grand potential and other thermodynamic functions. The multiplicative properties of partition functions and the extensivity of the corresponding potentials apply also to a single system when it is regarded as a set of spatially disjoint subdivisions in thermal contact.

A further extension of these ideas is possible even for subsystems of a body which are not spatially separable. This arises when the degrees of freedom in the body can be grouped into sets which interact with each other only very weakly compared to the interactions within the sets. It is then permissible to consider that each subset of dynamical variables, labelled by \( q, q = 1 \to Q \), has its own Hamiltonian and its own spectrum of eigen-energies \( \epsilon_q \). A typical total energy eigenvalue is written as

\[ E = \sum_q \epsilon_q \]  \quad (375)

and, if all degrees of freedom are in mutual equilibrium at temperature \( T = 1/k_B T \), the partition function \( Z = \sum_E \exp [-\beta E] \) factorises in the form

\[ Z(\beta) = \prod_q Z_q(\beta). \]  \quad (376)

Hence, under these conditions, each subset contributes additively to the entropy, energy and thermal capacity since they all depend on \( \ln [Z(\beta)] \).
One example of this is a metallic body for which, to a large extent, we can discuss separately
the vibrations of the crystal lattice, the motion of the free electrons through the system and
the atomic and nuclear spin variables. Another good example is a molecular gas, in which the
kinetic motion of the molecules, and their electronic, vibrational, rotational and spin degrees
of freedom, are only weakly coupled. The residual small interactions are, of course, necessary
for the attainment of a complete thermodynamic equilibrium, but they can often be ignored in
explanations of the gross characteristics of thermal behaviour in a physical system.

The experimental utility of these simple observations lies mainly in the fact that contributions
of the various quasi-independent subsystems of a body to its thermal properties very often become
separately important in different ranges of temperature. Measurement of thermal capacity, over
a wide interval of \( T \), frequently provides valuable information on several types of microscopic
structure.

### 6.3 Expected deviations

The main assumption connecting the statistical theory with macroscopic thermodynamics is that
mean value estimates of observable quantities can be identified with the experimentally repro-
ducible values. It is clearly necessary therefore that expected deviations from the estimated
numbers should be small. We start the investigation of this point by indicating how it can hap-
pen that observables like the total energy usually possess well-defined mean values even under
isothermal conditions. That is, we wish to explain why a macroscopic system, with definite tem-
perature, retains a reproducibly constant energy when in contact with a heat reservoir, in spite
of the possibility of energy transfer.

The canonical description of a system at isothermal equilibrium assigns a probability \exp\left(-E_j/k_B T\right)/Z(T)
to the occurrence of an energy eigenstate with eigenvalue \( E_j \), so the *most probable* state is always
the ground state, whatever the temperature. This does not lead to a useful estimate of the ob-
servable energy. The reason is that energy measurement always has some error associated with
it, so we should ask instead what is the summed probability for finding eigenstates with energies
in a small interval $\Delta E_k$, surrounding an energy value $\bar{E}_k$. As in the preceding subsection, we write $\Omega(\bar{E}_k)$ for the number of such states near $\bar{E}_k$, each with probability $\exp(-\bar{E}_k/k_B T)/Z(T)$. The total probability of finding such a state with energy in the interval $\Delta E_k$ is then given by $\Omega(\bar{E}_k)\exp(-\bar{E}_k/k_B T)/Z(T)$. For a macroscopic system the number $\Omega(\bar{E}_k)$ is a very rapidly increasing function of $\bar{E}_k$. On multiplying it by the decreasing exponential factor, we find that the grouped probability expression will have its maximum value well away from the ground state energy, except at the very lowest temperatures. This maximum is so extremely sharply peaked as a function of energy that the resulting estimate of the energy most likely to be observed can just as well be replaced by the mean value expression

$$\bar{E} = \sum_j E_j \frac{\exp(-\bar{E}_j/k_B T)}{Z(T)} \approx \sum_k \bar{E}_k \Omega(\bar{E}_k) \frac{\exp(-\bar{E}_k/k_B T)}{Z(T)}.$$  \hfill (377)

The expected deviation then measures the reliability of this estimate.

The simple calculation required has already been given in our treatment of energy transfer between bodies at different temperatures, but will be repeated here for convenience. We revert to the notation $\beta = 1/(k_B T)$ for the temperature parameter and write

$$\bar{E}(\beta) = \sum_j E_j \exp(-\bar{E}_j/k_B T) \frac{1}{Z(T)} = -\frac{\partial \ln[Z(\beta)]}{\partial \beta}. \hfill (378)$$

We also employ the convention of taking the zero of energy as that of an empty cavity which would exactly enclose the system so that, at constant values of the intensive parameters, $\bar{E}$ is proportional to $N$, the particle number. The mean square deviation of the energy from the average is now

$$(\Delta E)^2 = \sum_j \frac{(E_j - \bar{E})^2 \exp(-\beta E_j)}{Z} \approx \sum_j E_j^2 \exp(-\beta E_j) - \bar{E}^2. \hfill (379)$$

Differentiating Eq.(378) with respect to $\beta$ we find

$$-\frac{\partial \bar{E}}{\partial \beta} = \sum_j \frac{E_j^2 \exp(-\beta E_j)}{Z} + \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta}\right) \sum_j E_j \exp(-\beta E_j), \hfill (380)$$

which shows, using Eq.(38) again, that

$$-\frac{\partial \bar{E}}{\partial \beta} = \frac{\sum_j E_j^2 \exp(-\beta E_j)}{Z} - \bar{E}^2 \hfill (381)$$
From Eqs.(379) and (381) we deduce that

\[(\Delta E)^2 = \frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln [Z]}{\partial \beta^2} \tag{382}\]

and we see that yet another physically significant quantity is derivable from a knowledge of the partition function. A measure of the reliability of our energy estimate in Eq.(377) is now provided by the square of the relative energy deviation, i.e.,

\[\frac{(\Delta E)^2}{\bar{E}^2} = -\left( \frac{1}{\bar{E}^2} \right) \frac{\partial \bar{E}}{\partial \beta} = \left( \frac{k_B T^2}{\bar{E}^2} \right) \frac{\partial \bar{E}}{\partial T}, \tag{383}\]

which has been expressed in terms of \(\partial \bar{E}/\partial T = C_V\), the thermal capacity of the body at constant volume.

Since the \(T\) is independent of the size of the system and \(\bar{E}\) is extensive, we can conclude from its definition that the thermal capacity will be proportional to \(N\). The relative energy deviation must therefore satisfy

\[\frac{\Delta E}{\bar{E}} \propto \frac{1}{\sqrt{N}}. \tag{384}\]

For macroscopic systems, which have \(N = 10^{22}\) or greater, we can safely conclude that deviations from the estimated average will be negligible. A similar argument shows that the expected energy deviation given by the grand canonical method for a macroscopic body is also small compared to the mean energy. The result for \((\Delta E)^2\) has the same form as above, i.e.,

\[(\Delta E)^2 = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln [\Xi]}{\partial \beta^2} \tag{385}\]

where \(\Xi\) is the grand partition function. It gives again a result of the form of Eq.(384), though with \(N\) replaced by the mean particle number \(\bar{N}\).

When using the grand canonical method we should also check that expected deviations away from the calculated mean particle number \(\bar{N}\) are small, so that our results correspond to reproducible observables. We have that

\[\beta \bar{N} = \beta \sum_{N,j} N \exp \left[ -\beta (E_j - \mu N) \right] / \Xi = \frac{\partial \ln [\Xi]}{\partial \mu}, \tag{386}\]
while the mean square deviation is easily shown to be given by

$$\beta^2 (\Delta N)^2 = \beta^2 \frac{\partial \bar{N}}{\partial \mu} = \frac{\partial^2 \ln [\Xi]}{\partial \mu^2},$$  \hspace{1cm} (387)

where the steps in the derivation parallel those given for the energy in the canonical method and the grand partition function is defined by

$$\Xi = \sum_{N,j} \exp [-\beta \{ E_j(N) - \mu N \}].$$  \hspace{1cm} (388)

Finally, since \(\mu\) and \(\beta\) are both intensive quantities and \(\bar{N}\) is clearly extensive, we can quickly deduce that

$$\frac{\Delta N}{\bar{N}} \propto \frac{1}{\sqrt{N}},$$  \hspace{1cm} (389)

which is completely negligible for a macroscopic system.

Similar considerations apply to estimates of other extensive quantities and generally support the reliability of statistical calculations. It is also of some interest that expected deviations from the calculated mean values of intensive properties like the pressure can be disregarded. As a by-product of the discussions in the next subsection we shall show that the mean square deviation of the pressure away from its average value \(\bar{P}\) is given by

$$\sum_j (P_j - \bar{P})^2 p_j = (\Delta P)^2 = \frac{(\kappa_a - \kappa_\beta)}{\beta V},$$  \hspace{1cm} (390)

\(\kappa_a\) and \(\kappa_\beta\) being, respectively, the adiabatic and isothermal bulk moduli of the body. A bulk modulus is defined by \(\kappa = -V (\partial \bar{P}/\partial V)\), the inverse of the corresponding compressibility, and is clearly intensive. Since \(\beta\) is also intensive, while the volume \(V\) is extensive, we see that \((\Delta P)^2\) must be proportional to \(1/N\). The estimated relative deviation of the pressure thus takes on the now familiar standard form

$$\frac{\Delta P}{\bar{P}} \propto \frac{1}{\sqrt{N}},$$  \hspace{1cm} (391)

We remark in passing that the result in Eq.(390) shows that the adiabatic modulus is always greater than the isothermal modulus, since \((\Delta P)^2\) is by definition strictly positive for a system having two or more eigenstates with non-zero probability.
The arguments do sometimes fail for systems near to a phase change. One example is a fluid kept at the constant temperature and pressure which mark a point of transition between liquid and vapour. The heat capacity has a singular behaviour under these conditions and there will be large and uncontrollable fluctuations in the energy and volume. Another breakdown of the statistical method occurs in the treatment of an ideal Bose gas below a critical temperature. Macroscopic numbers of particles can condense into their ground states and the grand canonical formalism has to be modified in order to describe the situation adequately. But, apart from such special conditions, the validity of the statistical estimation of reproducible observables is backed up by a vast mass of experience.

6.4 Slow adiabatic changes

We turn now to another and more fundamental application of the formalism of error estimation. The problem to be discussed concerns a crucial link between thermodynamics and statistical mechanics. It is worth a careful look since, if not resolved, it throws into doubt the whole statistical foundation of thermal physics.

The question at issue is whether quasi-static and reversible adiabatic processes are also isentropic. Processes which are both adiabatic and isentropic are easily definable in pure thermodynamics and are routinely assumed to be possible. They appear, for example, as components of the Carnot cycle used to set up an absolute temperature scale independent of particular substances and are thus vital to the phenomenological theory. But it is not at all clear that the assumption of their existence for an arbitrary system is consistent with quantum mechanics and with our basic statistical interpretation of entropy as maximised uncertainty.

The potential difficulty arises from our microscopic explanation of the Second Law of Thermodynamics. We showed in section 5, in all generality, that an arbitrary adiabatic process could never decrease the maximised uncertainty, i.e., the entropy of a body; but this still leaves open the possibility of adiabatic changes in which the entropy is unaltered. Here we will investigate the matter again and show that, even under the most favourable conditions of quasi-static change, an
adiabatic process will almost always increase the entropy.

For definiteness, we shall consider a thermally isolated system of fixed particle number \( N \) whose thermodynamic state at equilibrium is adequately described in terms of the variables \( S, \bar{E}, \bar{P}, T \) and \( V \). It will be assumed that changes from an initial equilibrium state are induced by externally controlled variations of the volume \( V \) which cause work to be done on, or by, the system.

In thermodynamics the differences in the variables describing nearby equilibrium states satisfy the fundamental equation

\[
\delta \bar{E} = T \delta S - \bar{P} \delta V \tag{392}
\]

to first order in quantities \( \delta x \) which represent small but finite changes in the parameters \( x \). This follows also from the statistical formalism if we identify \( S \) with the maximised uncertainty, multiplied by Boltzmann’s constant. To connect this with dynamics it is assumed in addition that a system can be brought from one equilibrium state to another by means of a quasi-static and reversible process, during which the system remains effectively in equilibrium at all times. This is a slightly vague notion which becomes sharp only in the limit of infinitesimally slow changes. Under these conditions, \( -\bar{P} \delta V \) can be interpreted as the work done on the system in each stage of the process, while \( T \delta S \) is taken to represent the heat added, their sum giving the increment \( \delta \bar{E} \) in the internal energy. (It should be noted that these interpretations are not allowable for any other kind of process, though Eq.(392) is generally valid for initial and final states of equilibrium. The difference is that \( T \delta S \) and \( \bar{P} \delta V \) can then no longer be regarded as heat and work terms.)

However, for a quasi-static, reversible process performed on a thermally isolated body, the condition of zero heat transfer is always assumed to imply that \( \delta S = 0 \) in all intermediate steps. Thus, from Eq.(392), we deduce that the system should obey the differential equation

\[
\left( \frac{\partial \bar{E}}{\partial V} \right)_S = -\bar{P}, \tag{393}
\]

which can be integrated to give the final energy in terms of the initial energy and the values of \( \bar{P} \) along the adiabatic path. It is also possible to obtain, from pure thermodynamics, a differential
equation describing the change of temperature along the path, in terms of other observables. The result is

\[
\frac{\partial T}{\partial V}_S = - \left( \frac{T}{C_V} \right) \left( \frac{\partial \tilde{P}}{\partial T} \right)_V,
\]

where \(C_V\) is the thermal capacity of the body at constant volume, but for our purposes it is not necessary to give the derivation of this.

The entropy of the final state is, of course, the same as in the initial state since \(\delta S\) has been set equal to zero in the intervening steps. Thus in thermodynamics the given description of quasi-static, reversible and adiabatic processes seems to imply the conservation of entropy. All this is perfectly consistent with the Second Law, which claims only that an adiabatic change can not decrease the entropy. But the isentropic nature of this special process is far from obvious when we consider it from the point of view of quantum mechanics, yet require to maintain our previous microscopic interpretation of the entropy.

The quantum treatment of such processes relies on Ehrenfest’s Principle, also called, somewhat confusingly, the Adiabatic Theorem[27]. This says that if a pure work process, as described by a time-dependent modification of the Hamiltonian, is performed slowly enough, then any initial eigenstate of energy will remain at later times an eigenstate of the slowly varying energy operator. We will not pause here to give the rather lengthy proof of this result, but merely note that it is plausible. The point of this theorem for statistical mechanics is that during such quasi-static and adiabatic variations our initial state of knowledge about the system is preserved. At the start, the equilibrium state is described by assigning canonical probabilities to the possible energy eigenstates. At the end, each possible eigenstate will have evolved smoothly and uniquely from a definite initial eigenstate, there will have been no quantum transitions to neighbouring states and we can assign the new canonical probabilities from a knowledge of the final mean energy. The important observation now is that, according to the quantum theory, the final mean energy can be estimated by using the initial probabilities associated with the varying but smoothly connected eigenstates, since nothing in the process we have described suggests any revision of those probabilities. The initial and final uncertainties about which state occurs will thus be equal.
and, at first sight, this seems to confirm that the entropy will be unchanged.

The difficulty is that entropy is taken as the maximised uncertainty of a final equilibrium state and is based solely on the observable data for that state. Thus, in spite of being able to obtain the final mean energy from the initial probabilities and the final eigen-energies, there is no reason to believe that the canonical probability of any final state will be equal to the probability of the uniquely corresponding initial state. But if they are not all equal then the final maximised uncertainty will inevitably be larger than the initial uncertainty and this, according to our microscopic interpretation, implies greater entropy.

In order to see this more clearly, consider an initial equilibrium state of volume $V$ and temperature parameter $\beta = 1/(k_B T)$, with energy eigenstates and eigenvalues $|\psi_j(V)\rangle$ and $E_j(V)$, canonical probabilities

$$p_j(V, \beta) = \frac{\exp\left[-\beta E_j(V)\right]}{Z(V, \beta)},$$

and mean energy

$$\bar{E}(V, \beta) = \sum_j p_j(V, \beta) E_j(V).$$

At the end of a slow adiabatic process the volume will have a different value, say $V_F$, and the smoothly evolved eigenstates and eigenvalues will be $|\psi_j(V_F)\rangle$ and $E_j(V_F)$; but, from the quantum theorem, the probabilities of the states can be carried over unchanged. The final average energy of the body can thus be reliably represented by

$$\bar{E}_F(V_F) = \sum_j p_j(V, \beta) E_j(V_F).$$

Application of the usual statistical method, assuming the above value of $\bar{E}_F$, will result in the assignment of equilibrium canonical probabilities for the final states in the form

$$p_j(V_F, \beta_F) = \frac{\exp\left[-\beta_F E_j(V_F)\right]}{Z(V_F, \beta_F)},$$

in which the final temperature $T_F = 1/(k_B \beta_F)$ is related to the energy by

$$\bar{E}_F(V_F) = \sum_j p_j(V_F, \beta_F) E_j(V_F) = -\frac{\partial \ln[Z(V_F, \beta_F)]}{\partial \beta_F}.$$
Now we saw in subsection 5.2 that, given the same data values, a proposed probability distribution \( \{q_j\} \) has the maximum uncertainty only if every \( q_j \) equals the corresponding canonical probability \( p_j \). Since the Eqs.(397) and (399) say that the initial state probabilities and the final canonical distribution are both consistent with the same final value of the energy, \( \bar{E}_F(V_F) \), we deduce that the entropy will be unchanged after a slow adiabatic process only if, for every \( j \),

\[
p_j(V, \beta) = p_j(V_F, \beta_F).
\]

Using Eqs.(395) and (398), this implies that for any two pairs of corresponding states, labelled by \( j \) and \( k \), the energy eigenvalues should obey

\[
\beta_F[E_j(V_F) - E_k(V_F)] = \beta[E_j(V) - E_k(V)],
\]

i.e., that the energy spectrum at the end becomes uniformly expanded or compressed in the ratio \( \beta/\beta_F \) relative to the initial spectrum. It should be abundantly clear that this will not happen in general, since for an arbitrary system the initial and final spectra are completely determined by the microscopic structure. An interesting exception is the ideal gas, in which the energy eigenvalues are all proportional to \( 1/V^{2/3} \), so that the equations can be satisfied by choosing \( \beta_F = \beta(V_F/V)^{2/3} \).

For almost all other systems, there is no single value of \( \beta_F \) which can ensure the truth of Eq.(401). We conclude that Eq.(400) can not hold for all \( j \), and hence that the entropy will have increased.

Even more disturbingly, we see that there is something inconsistent in the notion of adiabatic reversibility. If the process causes the entropy to increase as we go from \( V \) to \( V_F \), then reversibility should imply that the entropy will decrease to its initial value as we return to volume \( V \). But we have shown that this is certainly not possible in any adiabatic change, since such a result would contravene the Second Law.

The only conceivable way out of these difficulties is to attempt to show that the entropy increase in a slow but finite work process is generally negligible. A consideration of the extreme sharpness of the statistical estimates of thermodynamic variables provides a clue in this direction. After an adiabatic change, the overwhelming concentration of probability attaches to eigenstates with energies near to the final mean energy \( \bar{E}_F \). It is therefore quite plausible that the final
canonical distribution in that region could be a good approximation to the canonical probabilities for corresponding states at the beginning of the process, which, as seen earlier, should lead to a reliable prediction of the final energy.

To support this idea we need to derive explicit estimates for changes in the observables when the volume \( V \) of a thermally isolated body is varied by a small but finite amount \( \delta V \). We shall use the notation \((Dx)_a\) for the adiabatic increment of a quantity \( x \), expanded up to order \((\delta V)^2\) in the slowly varied control parameter \( V \). The term adiabatic here refers to the quantum description and implies that evaluation of \((Dx)_a\) is always to be based on energy changes obtained by holding the eigenstate probabilities constant at their initial values.

Starting as before with an internal equilibrium state of mean energy \( \bar{E} \), volume \( V \) and canonical temperature parameter \( \beta \), the adiabatic change in energy, induced by a small modification of volume, is represented by

\[
(D\bar{E})_a = \left( \frac{\partial \bar{E}}{\partial V} \right)_a (\delta V) + \frac{1}{2} \left( \frac{\partial^2 \bar{E}}{\partial V^2} \right)_a (\delta V)^2. \tag{402}
\]

According to our assumptions, this expression can be interpreted in two different ways which, for consistency, must agree.

By the adiabatic quantum theorem, the possible energy states and eigenvalues will move smoothly to the new ones and corresponding states will retain their initial canonical probabilities

\[
p_j(\beta, V) = \exp \left[ -\beta E_j(V) - \ln Z \right].
\]

Hence, with fixed \( \beta \) and \( V \) in \( p_j(\beta, V) \), the change in \( \bar{E} = \sum_j E_j(V)p_j \) can be estimated from the increments in the \( E_j(V) \) alone, i.e.,

\[
(D\bar{E})_a = \left[ \sum_j \left( \frac{\partial E_j}{\partial V} \right)_p \right] (\delta V) + \frac{1}{2} \left[ \sum_j \left( \frac{\partial^2 E_j}{\partial V^2} \right)_p \right] (\delta V)^2. \tag{403}
\]

Since the pressure in state \( |\psi_j(V)\rangle \) is \( P_j = -\partial E_j/\partial V \), the coefficient of \( \delta V \) is just \( -\bar{P} \), where \( \bar{P} = \sum_j P_j p_j \) is the initial mean pressure. Comparison with Eq.(393) then shows that, at the start of the process, we have

\[
\left( \frac{\partial \bar{E}}{\partial V} \right)_a = -\bar{P} = \left( \frac{\partial \bar{E}}{\partial V} \right)_S, \tag{404}
\]

and we see that the quantum description of quasi-static adiabatic change leads to exactly the same initial value of the derivative as the thermodynamic account, which is based on the assumption

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that the entropy stays constant. This state of affairs does not hold for higher derivatives and we shall show that discrepancies between quantum statistical theory and ordinary thermodynamics appear already in the next order.

Using the canonical probability formula \( p_j = \exp\left[-\beta E_j(V) - \ln Z(\beta, V)\right] \), the summation in the second term of Eq.(403) can be rewritten as follows

\[
\sum_j \left( \frac{\partial^2 E_j}{\partial V^2} \right) p_j = \left( \frac{\partial[\sum_j (\partial E_j/\partial V)p_j]}{\partial V} \right)_\beta - \sum_j \left( \frac{\partial E_j}{\partial V} \right) \left( \frac{\partial p_j}{\partial V} \right)_\beta
\]

\[
= - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta + \beta \sum_j P_j(P_j - \bar{P})p_j
\]

\[
= - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta + \beta \sum_j (P_j - \bar{P})^2 p_j,
\]

(405)

where we have obtained the second equality from the usual definitions of \( P_j \) and \( \bar{P} \) and have also recalled the results \( \beta \bar{P} = (\partial \ln Z/\partial V)_\beta \). The last form comes from the obvious substitution of \( (P_j - \bar{P}) \) for the factor \( P_j \) in the second term, which is clearly allowable since \( \sum_j \bar{P}(P_j - \bar{P})p_j = 0 \).

Hence, on writing \( (\Delta P)^2 \) for the mean square pressure deviation, we find that

\[
(D\tilde{E})_a = -\bar{P}\delta V + \frac{1}{2} \left[ \beta(\Delta P)^2 - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta \right] (\delta V)^2.
\]

(406)

The alternative way of viewing the expression for \( (D\tilde{E})_a \) is to employ our basic statistical assumption that the intervening equilibrium states can be described by canonical distributions with varying \( \beta \) values. Thus, for consistency to first order, we should be able to write

\[
\left( \frac{\partial \tilde{E}}{\partial V} \right)_a = \left( \frac{\partial \tilde{E}}{\partial V} \right)_\beta + \left( \frac{\partial \tilde{E}}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial V} \right)_a = -\bar{P}.
\]

(407)

This gives a useful formula for the initial adiabatic derivative of the canonical temperature. From the definition \( \tilde{E}(\beta, V) = \sum_j E_j(V)p_j(\beta, V) \) we get

\[
\left( \frac{\partial \tilde{E}}{\partial V} \right)_\beta = \sum_j \left( \frac{\partial E_j}{\partial V} \right)_\beta p_j + \sum_j E_j \left( \frac{\partial p_j}{\partial V} \right)_\beta
\]

\[
= -\bar{P} + \beta \sum_j (E_j - \bar{E})(P_j - \bar{P})p_j
\]

\[
= -\bar{P} + \beta \langle (\Delta E)(\Delta P) \rangle,
\]

(408)

where \( \langle (\Delta E)(\Delta P) \rangle \) denotes the expected value of the products of pressure and energy deviations.
We also know from Eq.(397) of the last subsection that
\[
\left( \frac{\partial \bar{E}}{\partial \beta} \right)_V = - \sum_j (E_j - \bar{E})^2 p_j = -(\Delta E)^2.
\] (409)

Substituting Eqs.(408) and (409) into Eq.(407) now yields
\[
\left( \frac{\partial \beta}{\partial V} \right)_a = \beta \langle (\Delta E)(\Delta P) \rangle \left( \frac{\partial \bar{P}}{\partial \beta} \right)_V.
\] (410)

Under the statistical interpretation of measured quantities, this agrees with the thermodynamic result for quasi-static and adiabatic temperature change quoted in Eq.(394). Such agreement is to be expected since the quantum theory and the isentropic assumption of ordinary thermodynamics both lead to the initial value of the volume derivative of \( \bar{E} \) being equal to \(-\bar{P}\), as recorded in Eq.(404). It should be noted, however, that Eq.(410) holds only at the initial state.

The second order volume derivatives of \( \bar{E} \) are not in general equal in the two theories. In the quantum treatment we have from Eq.(406) that
\[
\left( \frac{\partial^2 \bar{E}}{\partial V^2} \right)_a = - \left( \frac{\partial \bar{P}}{\partial \beta} \right)_a = \beta (\Delta P)^2 - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta,
\] (411)

while the corresponding derivative taken at constant entropy is given by
\[
\left( \frac{\partial^2 \bar{E}}{\partial V^2} \right)_S = - \left( \frac{\partial \bar{P}}{\partial \beta} \right)_S = - \left( \frac{\partial \bar{P}}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial V} \right)_S - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta.
\] (412)

A simple manipulation, using the definition \( \bar{P} = \sum_j P_j p_j \), quickly shows that \( (\partial \bar{P}/\partial \beta)_V = -\langle (\Delta E)(\Delta P) \rangle \). Also, since \( (\partial \beta/\partial V)_S = (\partial \beta/\partial V)_a \), as mentioned above, we can use Eq.(410) to rewrite Eq.(412) in the form
\[
- \left( \frac{\partial \bar{P}}{\partial V} \right)_S = \beta \langle (\Delta E)(\Delta P) \rangle \left( \frac{\partial \bar{P}}{\partial \beta} \right)_V - \left( \frac{\partial \bar{P}}{\partial V} \right)_\beta.
\] (413)

Comparison of Eqs.(411) and (413) now leads to a necessary condition for complete agreement between the quantum and thermodynamic descriptions of quasi-static and adiabatic processes, namely, that we should have
\[
(\Delta P)^2 - \frac{\langle (\Delta E)(\Delta P) \rangle^2}{(\Delta E)^2} = 0.
\] (414)

The expression in Eq.(414) is related to the correlation coefficient for energy and pressure and it can vanish exactly only if \( P_j = aE_j + b \) for all \( j \), where \( a \) and \( b \) are independent of \( j \).
is almost certainly not true for real bodies, but the undoubted success of thermodynamics does seem to imply that the condition holds approximately, with both terms small.

We remark at this point that Eq. (411) provides the justification for our estimate of the $N$-dependence of the relative pressure deviation given at the end of the last subsection. Since any bulk modulus of a body is defined by $\kappa = -V(\partial P/\partial V)$, we have immediately that the difference of adiabatic and isothermal bulk moduli is related to the expectation value of the square pressure deviation by

$$\frac{(\kappa_a - \kappa_\beta)}{\beta V} = (\Delta P)^2, \quad (415)$$

which shows clearly that $(\Delta P)$ is proportional to $1/\sqrt{N}$. It is also worthy of remark that $(\Delta P)^2$ cannot be calculated by differentiation of $\ln Z$, so that we have at last a quantity that is not accessible from knowledge of the partition function alone. All observables of ordinary thermodynamics are directly related to $\ln Z$ and we see that the quantum version of the adiabatic bulk modulus must differ from the thermodynamic version which is evaluated at constant entropy. Indeed, this analogue of Eq. (415) coming from thermodynamics can be read off from Eq. (413) and takes the form

$$\frac{(\kappa_a - \kappa_\beta)}{\beta V} = \frac{\langle (\Delta E)(\Delta P) \rangle^2}{(\Delta E)^2}. \quad (416)$$

This is derivable from $\ln Z$, but does not lead to an estimate of $(\Delta P)/\bar{P}$.

We have now developed all the equations necessary for the evaluation of the change in the entropy to second order in the volume increment $\delta V$. We start from the uncertainty expression

$$\sigma(V, \beta) = \beta \bar{E}(V, \beta) + \ln [Z(V, \beta)], \quad (417)$$

and require to calculate the differential coefficients in the formula

$$(D\sigma)_a = \left(\frac{\partial \sigma}{\partial V}\right)_a (\delta V) + \frac{1}{2} \left(\frac{\partial^2 \sigma}{\partial V^2}\right)_a (\delta V)^2. \quad (418)$$

The adiabatic subscript implies that the derivatives are to be computed from the changes in energy $\bar{E}$ and effective canonical temperature $\beta$ which are given by the quantum description of the process. It is also implied that these coefficients denote rates of change evaluated at the initial equilibrium values of the parameters $V$ and $\beta$. 

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The first adiabatic derivative of $\sigma$ is given by

$$
(\frac{\partial \sigma}{\partial V})_a = \beta \left( \frac{\partial \bar{E}}{\partial V} \right)_a + \bar{E} \left( \frac{\partial \beta}{\partial V} \right)_a + \left( \frac{\partial \ln Z}{\partial V} \right)_\beta + \left( \frac{\partial \ln Z}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial V} \right)_a
$$

(419)

Since $\left( \frac{\partial \ln Z}{\partial \beta} \right)_V = -\bar{E}$ and, by hypothesis, the adiabatic variation of $\bar{E}$ can be represented by using a canonical distribution with suitably chosen $\beta$, the second and fourth terms in Eq.(419) will cancel at all stages of the process. Similarly, we can use the relation $\left( \frac{\partial \ln Z}{\partial V} \right)_\beta = \beta \bar{P}$, where $\bar{P}$ is the canonically estimated pressure at any stage, to obtain the result

$$
(\frac{\partial \sigma}{\partial V})_a = \beta \left[ \left( \frac{\partial \bar{E}}{\partial V} \right)_a + \bar{P} \right].
$$

(420)

We shall consider the implications of this more generally below, but for the moment we note only that the initial state adiabatic derivative of $\bar{E}$ has been shown in Eq.(404) to be given by $(\partial \bar{E}/\partial V)_a = -\bar{P}$, in which $\bar{P}$ is now the initial pressure. Hence the starting value of $(\partial \sigma/\partial V)_a$ is zero.

Differentiating again, the second adiabatic derivative takes the form

$$
\left( \frac{\partial^2 \sigma}{\partial V^2} \right)_a = \left( \frac{\partial \beta}{\partial V} \right)_a \left[ \left( \frac{\partial \bar{E}}{\partial V} \right)_a + \bar{P} \right] + \beta \left[ \left( \frac{\partial^2 \bar{E}}{\partial V^2} \right)_a + \left( \frac{\partial \bar{P}}{\partial V} \right)_a + \left( \frac{\partial \bar{P}}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial V} \right)_a \right].
$$

(421)

The expression in square brackets in the first term of Eq.(421) again has the initial value of zero and we can substitute in the second term the initial value results recorded in Eqs.(410) and (411), together with the expression for $(\partial \bar{P}/\partial \beta)_V$ given immediately after Eq.(412). Inserting these derivatives into Eq.(418), we find, to order $(\delta V)^2$ in volume change, that the increment of uncertainty over its original value is given by

$$
(D\sigma)_a = \left( \frac{\beta^2}{2} \right) \left[ (\Delta P)^2 - \frac{\langle (\Delta E)(\Delta P) \rangle^2}{(\Delta E)^2} \right] (\delta V)^2.
$$

(422)

This is our basic result for slow adiabatic processes and we deduce once again that a necessary condition for them to be also isentropic is that

$$
(\Delta P)^2 - \frac{\langle (\Delta E)(\Delta P) \rangle^2}{(\Delta E)^2} = 0
$$

(423)

For real systems, however, it can easily be shown that the expression on the left hand side of Eq.(423) has a value greater than zero. Denoting it by $D$ and using the transcriptions of the
expectation values in terms of the initial canonical probabilities, we soon find that it takes the form

\[ D = \left[ \frac{1}{(\Delta E)^4} \right] \sum_j \left[ (P_j - \bar{P})(\Delta E)^2 - (E_j - \bar{E})(\langle \Delta E \rangle (\Delta P)) \right]^2 p_j. \]  

(424)

This is a sum of squares weighted by the eigenstate probabilities and is thus strictly positive unless every square vanishes, that is, for all \( j \),

\[ (P_j - \bar{P})(\Delta E)^2 - (E_j - \bar{E})(\langle \Delta E \rangle (\Delta P)) = 0. \]  

(425)

We have here an exact version of the linear relation between pressures and energies, mentioned after Eq.(414), which is required to hold if the statistical and thermodynamic descriptions are to agree. It is extremely unlikely that Eqs.(425) are valid for any real system. On the other hand, it is quite plausible that among all eigenstates which carry appreciable probability the overwhelming majority will have values of \( P_j \) and \( E_j \) very close to the respective mean values \( \bar{P} \) and \( \bar{E} \). We have indeed argued from the beginning that this must be true if statistical mechanics is to have any hope of providing sharply defined estimates of macro-variables. This applies, of course, only to reproducible properties of a system, but the observed pressures and energies certainly fall into that category, so we expect that the criterion in Eq.(423) will be satisfied to quite adequate approximation. We conclude that for all practical purposes the increase of entropy in a slow adiabatic process can be neglected.

The above argument is almost, but not entirely, convincing as a solution to this special problem of reconciling statistical theory with accepted results of thermodynamics, since there could conceivably be surprises in higher orders of the type of calculation just given. It is therefore of some interest to show that linear relations between the pressures \( P_j \) and energies \( E_j \) are in fact sufficient, as well as necessary, conditions for a quasi-static and adiabatic change to be isentropic.

To see this, we go back to Eq.(420), which holds throughout the process, and recall that the quantum mechanical estimate of the mean energy is always represented by

\[ \bar{E}(V) = \sum_j E_j(V)p_j(V, \beta_I), \]  

(426)
at all $V$, with the probabilities being held at their initial equilibrium values $p_j(I)$. As the volume is varied, the value of $\bar{E}(V)$ is used at each stage to set up a new canonical distribution $\{p_j(V,\beta)\}$ by maximising the uncertainty. The varying pressure can then be estimated from the formula

$$\bar{P}(V,\beta) = \sum_j P_j p_j(V,\beta).$$

Substituting Eq.(426) into Eq.(420) we now find that

$$\left( \frac{\partial \sigma}{\partial V} \right)_a = \beta \sum_j [\bar{P}(V,\beta) - P_j(V)] p_j(V,\beta),$$

(427)

where we have used the result $P_j(V) = -\partial E_j(V)/\partial V$ and brought $\bar{P}$ inside the bracket by invoking the normalisation of the probabilities.

It is easy to see that the derivative will not vanish in general, except at the initial values of $V$ and $\beta$, since the probabilities used to define $\bar{P}$ will have changed from their starting values. But it is also obvious that a sufficient condition for it to vanish everywhere is that each $P_j$ is related to the corresponding eigenstate energy $E_j$ by $P_j(V) = a E_j(V) + b$, where $a$ and $b$ can depend on $V$ but not on $j$. This follows because the sum in Eq.(427) is then proportional to $\sum_j [\bar{E}(V) - E_j(V)] p_j(I)$, which is zero by the definition of an adiabatic process displayed in Eq.(426).

When the linear relation which is both necessary and sufficient for zero entropy change is not satisfied, the adiabatic derivative of $\sigma$ is either zero or positive (for increasing $V$). But segments of the adiabatic path must exist along which $(\partial \sigma/\partial V)$ is strictly positive, since the entropy will increase. Still, the underlying rationale of statistical mechanics does suggest very strongly that the slope of $\sigma$ is unlikely to grow large enough to be significant. The reason has already been given above and is just that most states likely to occur will have individual pressures $P_j$ which are very close in value to the mean pressure $\bar{P}(V,\beta)$ evaluated from the canonical distribution for the given $V$ and $\beta$. It if were not so, the formalism could not describe reproducible measurements. When it is so, the derivative will be small whatever the initial state probabilities. Assuming, then, that the adiabatic path does not cross a phase boundary, where large deviations are possible, we can ignore the entropy increase. The argument applies also for a decrease of $V$ from its initial value, in which case the proved increase of entropy implies that the derivative of $\sigma$ will be negative. The apparent discrepancy between thermodynamics and statistical mechanics has thus been effectively
It is, however, of some theoretical interest that the discrepancy occurs at all and a few final comments are in order. Just as the quantum theory estimate of the adiabatically changing energy is \( \bar{E}(V) = \sum_j E_j(V)p_j(I) \), the most reasonable estimate of the actual pressure exerted by the system at any stage is given by \( P(V) = \sum_j P_j(V)p_j(I) \), where \( P_j(V) = -\partial E_j(V)/\partial V \). This will in general be different from the mean pressure \( \bar{P}(V,\beta) \) derived using the canonical equilibrium probabilities at that volume, which have been assigned from the value of \( \bar{E}(V) \). We can now write Eq.(427) in the form

\[
\left( \frac{\partial \sigma}{\partial V} \right)_a = \beta[\bar{P}(V,\beta) - P(V)].
\] (428)

We know that for increasing \( V \) this is never negative and will in fact be positive on the average, so that \( P(V) \) is generally less than \( \bar{P}(V,\beta) \). The implication is that the actual external work done by the body during the expansion will be a little smaller than the work estimated canonically. If the body is compressed, then \( P(V) \) will on average be greater than the pressure \( \bar{P}(V,\beta) \), since the entropy must still increase, so the work done on the system will be slightly larger than the canonical estimate. In either case, the final energy of the system will be greater than that predicted from the isentropic assumption of thermodynamics.

We have thus shown that the terms \( T\delta S \) and \( P\delta V \) in Eq.(392) can not strictly be regarded as representing increments of heat and work in this special quasi-static process, though such an interpretation is adequate for most purposes. We have also seen that the process can not strictly be thought of as reversible. If the internal mechanics of the system were entirely under control then it would be possible to reverse any changes. But only a few macroscopic variables are reproducible enough for use in physics and even these are subject to measurement errors as well as fluctuations from their estimated mean values. The irreversibility arises because we are forced to supplement the mechanics with probability arguments, which are always such that uncertainty will increase as we move away from some initial equilibrium state. The uneasy blending of dynamics and inference has been a constant theme in statistical mechanics since its inception.
6.5 Classical formalism

All the expressions involving the canonical partition function $Z(V,\beta)$ or the grand canonical partition function $\Xi(V,\beta,\mu)$ were derived using the quantum theory and these functions are discrete sums over the quantum numbers of energy eigenstates. What happens when we go over to Classical Mechanics? There are then no quantum states and all dynamical quantities are continuous variables. In particular, the system energy can take on any value and we may therefore expect that our previous sums will be replaced by integrals.

BUT: How are we to define System States in Classical Mechanics?

One possibility is to specify all the coordinates necessary to describe the system together with all the corresponding momenta which define its state of motion. The set of current values of these quantities provide a label $j = \{x_i, p_i\}, i = 1, \ldots, 3N$, where $N$ is the number of particles. This denotes a point in what is called the phase space of the system and its variation in time gives a complete picture of the evolution of the body.

Thus the quantum energy state can be replaced by a phase function, i.e.,

$$E_{\text{quantum}}(j) \Rightarrow E_{\text{classical}}(\{x_i, p_i\}). \quad (429)$$

Now in classical mechanics the energy expressed in terms of coordinates and momenta is called the Hamiltonian of the system. Hence by analogy with the quantum treatment we can try to write the canonical formula as

$$\text{Probability} \propto \exp\left[-\frac{H(\{x_i, p_i\})}{k_B T}\right] \quad (430)$$

BUT: How are we to calculate the Number of States?

This problem must be solved before we can normalise the probabilities. The method, going back to Boltzmann, is to break up Phase-Space into small cells of Phase-Volume

$$d^{3N}xd^{3N}p \Rightarrow dx_1 \ldots dx_{3N}dp_1 \ldots dp_{3N}, \quad (431)$$
and assume that the number of states with values of \( \{x_i, p_i\} \) within this little hypercube is proportional to the given volume element. Hence for the normalisation constant of probability we are led to write

\[
Z = \sum_j \exp[-\beta E_j] \Rightarrow \int d^{3N} x d^{3N} p \exp[-\beta H(\{x_i, p_i\})].
\]  

(432)

To make the classical version of \( Z \) dimensionless we need to divide this integral by a suitable unit of phase-volume. Nothing suggests itself in classical theory, but the quantum theory of the kinetic motion of atoms does provide the natural unit \((2\pi\bar{\hbar})^{3N}\). Inserting this we get

\[
Z_{\text{classical}} = \int \frac{d^{3N} x d^{3N} p}{(2\pi\bar{\hbar})^{3N}} \exp[-\beta H(\{x_i, p_i\})].
\]

(433)

Most physical quantities that we require to calculate may be obtained from \( \ln[Z_{\text{classical}}] \), so the additive constant \( \ln[(2\pi\bar{\hbar})^{3N}] \) makes no difference.

But the constant is important when calculating the entropy and the other thermodynamic functions which depend directly on \( \ln[Z] \). So this remnant of quantum mechanics is still relevant for some purposes and the first versions of statistical mechanics only gave an answer for the entropy to a then unknown constant. Despite this, classical statistical theory was and is surprisingly successful in explaining many facts of thermal physics and usually only goes catastrophically wrong at very low values of the temperature and also where individual quantum effects in atoms or molecules are still important at room temperature. Historically, it was certain discrepancies between the classical calculations and observation of specific heats of gases and solids that provided strong clues to the presence of quantum phenomena.

Finally, in calculating the properties of gases, it turns out that there should be a further trace of quantum mechanics left in the formalism of classical statistics. The additive property of entropy is only obtained if \( \ln[Z_{\text{classical}}] \) contains a factor \((1/N!)\).
7 Conclusions

We have separated the principal concerns of statistical mechanics into two distinct problems - one concerning the treatment of probability and the other concentrating on the explicit mechanical aspects of the calculations. By taking a Bayesian view of the probability question we have shown that the development of the subject can be expressed in a highly logical fashion, much closer to the dictates of "common sense". To illustrate this point we have presented a didactic account of the probability calculus of Cox which is likely to be unfamiliar to many physicists but is ideal for this development and as such worthy of wider dissemination and a place in future textbooks.

Our main aim has been to make an unbiased assignment of probabilities by maximising Shannon’s information entropy

\[ \sigma(\{p_j\}) = - \sum_j p_j \ln(p_j), \]  

subject to the constraints implied by the data \( K \) and normalisation. We have then shown that this function \( \sigma_{\text{max}}(\{p(j|K)\}) \) possesses all the properties of the thermodynamic entropy \( S \). It is an extensive function of state, defined for equilibrium conditions, that does not decrease in adiabatic processes and is related experimentally to heat and temperature.

Once the identification of \( \sigma_{\text{max}} \) with the phenomenological entropy \( S \) was made it was possible to develop statistical mechanics from it and to re-derive many well known results and links to thermodynamics. We investigated the traditional microcanonical, canonical and grand canonical methods with the constraints on normalisation, mean energy and mean particle number accommodated by means of physically significant Lagrange multipliers. We not only found a maximum of the uncertainty function but demonstrated explicitly that it was indeed the absolute maximum of our entropy function.

In the course of further development we came upon one unexpected and truly startling result concerning the question of whether quasi-static and reversible adiabatic processes are also necessarily isentropic. The answer in traditional thermodynamics to this question is assumed to be definitively "yes". However, in our analysis it presents more subtle facets and is not a trivial point
to answer. We have found that such quasi-static, reversible processes, requiring the entropy to remain constant, are only possible if the final and initial energy eigenspectra scale in the ratio of the final to initial temperatures. Although this can be achieved in the simplest idealised systems such as the perfect gas, it is not generally possible for more complicated systems. We showed that it effectively requires the vanishing of the correlation coefficient between energy and pressure deviations, which can only happen if $P_j = aE_j + b$ for all states $j$.

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