Tony Guénault

# Statistical Physics

**Second and enlarged edition**
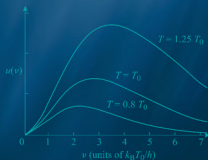


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Statistical Physics

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# Statistical Physics

## Second Revised and Enlarged Edition

by

## Tony Guénault

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# Preface

## Preface to the first edition

Statistical physics is not a difficult subject, and I trust that this will not be found a difficult book. It contains much that a number of generations of Lancaster students have studied with me, as part of their physics honours degree work. The lecture course was of 20 hours' duration, and I have added comparatively little to the lecture syllabus. A prerequisite is that the reader should have a working knowledge of basic thermal physics (i.e. the laws of thermodynamics and their application to simple substances). The book *Thermal Physics* by Colin Finn in this series forms an ideal introduction.

Statistical physics has a thousand and one different ways of approaching the same basic results. I have chosen a rather down-to-earth and unsophisticated approach, without I hope totally obscuring the considerable interest of the fundamentals. This enables applications to be introduced at an early stage in the book.

As a low-temperature physicist, I have always found a particular interest in statistical physics, and especially in how the absolute zero is approached. I should not, therefore, apologize for the low-temperature bias in the topics which I have selected from the many possibilities.

Without burdening them with any responsibility for my competence, I would like to acknowledge how much I have learned in very different ways from my first three 'bosses' as a trainee physicist: Brian Pippard, Keith MacDonald and Sydney Dugdale. More recently my colleagues at Lancaster, George Pickett, David Meredith, Peter McClintock, Arthur Clegg and many others have done much to keep me on the rails. Finally, but most of all, I thank my wife Joan for her encouragement.

*A.M. Guénault*
*1988*

## Preface to the second edition

Some new material has been added to this second edition, whilst leaving the organization of the rest of the book (Chapters 1–12) unchanged. The new chapters aim to illustrate the basic ideas in three rather distinct and (almost) independent ways. Chapter 13 gives a discussion of chemical thermodynamics, including something about chemical equilibrium. Chapter 14 explores how some interacting systems can still be treated by a simple statistical approach, and Chapter 15 looks at two interesting applications of statistical physics, namely superfluids and astrophysics.

The book will, I hope, be useful for university courses of various lengths and types. Several examples follow:

1. Basic general course for physics undergraduates (20–25 lectures): most of Chapters 1–12, omitting any of Chapters 7, 10, 11 and 12 if time is short;
2. Short introductory course on statistical ideas (about 10 lectures): Chapters 1, 2 and 3 possibly with material added from Chapters 10 and 11;
3. Following (2), a further short course on statistics of gases (15 lectures): Chapters 4–6 and 8–9, with additional material available from Chapter 14 and 15.2;
4. For chemical physics (20 lectures): Chapters 1–7 and 10–13;
5. As an introduction to condensed matter physics (20 lectures): Chapters 1–6, 8–12, 14, 15.1.

In addition to those already acknowledged earlier, I would like to thank Keith Wigmore for his thorough reading of the first edition and Terry Sloan for his considerable input to my understanding of the material in section 15.2.1.

*A.M. Guénault*
*1994*

# Preface to the revised and enlarged second edition

This third edition of Statistical Physics follows the organization and purpose of the second edition, with comparatively minor updating and changes to the text. I hope it continues to provide an accessible introduction to the subject, particularly suitable for physics undergraduates. Chapter summaries have been added to the first nine (basic) chapters, in order to encourage students to revise the important ideas of each chapter – essential background for an informed understanding of later chapters.

*A.M. Guénault*
*2007*

**A SURVIVAL GUIDE TO STATISTICAL PHYSICS**

*Chapter 1* Assembly of $N$ identical particles volume $V$, in thermal equilibrium at temperature $T$

are the particles weakly interacting?

YES — gaseous particles?

NO — *Chapter 12 or 14* could help *or* read a thicker book *or* give up!

gaseous particles?

NO — *Chapters 2,3* use Boltzmann statistics

$$n_j = \frac{N}{Z} \exp(-\varepsilon_j/k_B T)$$

partition function:
$$Z = \Sigma (-\varepsilon_j/k_B T)$$
all states

$$F = -N k_B T \ln Z$$

YES — *Chapters 4,5* is occupation number of each state $f \ll 1$?

i.e. is $A = \frac{N}{V}\left(\frac{h^2}{2\pi M k_B T}\right)^{3/2} \ll 1$?

YES — *Chapters 6,7* use MB statistics

$$f(\varepsilon) = \frac{N}{Z} \exp(-\varepsilon/k_B T)$$

$$Z = V \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}$$

for a monatomic gas

$$F = -k_B T \ln \left(\frac{Z^N}{N}\right)$$

NO — is $\Psi$ A or S?

A — *Chapter 8* use FD statistics

$$f(\varepsilon) = \frac{1}{\exp\{(\varepsilon - \mu)/k_B T\} + 1}$$

applies to odd-half integral spin particles (electrons, $^3$He, nucleons, some cold atoms)

S — *Chapter 9* use BE statistics

$$f(\varepsilon) = \frac{1}{B \exp\{\varepsilon/k_B T\} - 1}$$

applies to zero or integral spin particles (some cold atoms, $^4$He) Set $B = 1$ if no particle conservation (photons, phonons)

# 1

# Basic ideas

There is an obvious problem about getting to grips with an understanding of matter in thermal equilibrium. Let us suppose you are interested (as a designer of saucepans?) in the thermal capacity of copper at 450 K. On the one hand you can turn to thermodynamics, but this approach is of such generality that it is often difficult to see the point. Relationships between the principal heat capacities, the thermal expansion coefficient and the compressibility are all very well, but they do not help you to understand the particular magnitude and temperature dependence of the actual heat capacity of copper. On the other hand, you can see that what is needed is a microscopic mechanical picture of what is going on inside the copper. However, this picture becomes impossibly detailed when one starts to discuss the laws of motion of $10^{24}$ or so copper atoms.

The aim of statistical physics is to make a bridge between the over-elaborate detail of mechanics and the obscure generalities of thermodynamics. In this chapter we shall look at one way of making such a bridge. Most readers will already be familiar with the kinetic theory of ideal gases. The treatment given here will enable us to discuss a much wider variety of matter than this, although there will nevertheless be some limitations to the traffic that can travel across the bridge.

## 1.1 THE MACROSTATE

The basic task of statistical physics is to take a system which is in a well-defined thermodynamic state and to compute the various thermodynamic properties of that system from an (assumed) microscopic model.

The '*macrostate*' is another word for the thermodynamic state of the system. It is a specification of a system which contains just enough information for its thermodynamic state to be well defined, but no more information than that. As outlined in most books on thermal physics (e.g. Finn's book *Thermal Physics* in this series), for the simple case of a pure substance this will involve:

- the nature of the substance – e.g. natural copper;
- the amount of the substance – e.g. 1.5 moles;

- a small number of pairs of thermodynamic co-ordinates – e.g. pressure $P$ and volume $V$; magnetic field $B$ and magnetization $M$; surface tension and surface area, etc.

Each of these pairs is associated with a way of doing work on the system. For many systems only $P - V$ work is relevant, and (merely for brevity) we shall phrase what follows in terms of $P - V$ work only. Magnetic systems will also appear later in the book.

In practice the two co-ordinates specified, rather than being $P$ and $V$, will be those appropriate to the external conditions. For instance, the lump of copper might be at a specific pressure $P$ (= 1 atm) and temperature $T$ (= 450 K). In this case the macrostate would be defined by $P$ and $T$; and the volume $V$ and internal energy $U$ and other parameters would then all be determined in principle from $P$ and $T$. It is precisely one of the objectives of statistical physics to obtain from first principles what are these values of $V, U$, etc. (In fact, we need not set our sights as low as this. Statistical physics also gives detailed insights into dynamical properties, and an example of this is given in Chapter 12.)

Now comes, by choice, an important limitation. In order to have a concrete situation to discuss in this chapter (and indeed throughout the first eight chapters of this book), we shall concentrate on one particular type of macrostate, *namely that appropriate to an isolated system*. Therefore the macrostate will be defined by the nature of the substance, the amount, and by $U$ and $V$. For the isolated system in its energy-proof enclosure, the internal energy is a fixed constant, and $V$ is also constant since no work is to be done on the system. The (fixed) amount of the substance we can characterize by the number $N$ of microscopic 'particles' making up the system.

This limitation is not too severe in practice. For an isolated system in which $N$ is reasonably large, fluctuations in (say) $T$ are small and one finds that $T$ is determined really rather precisely by $(N, U, V)$. Consequently one can use results based on the $(N, U, V)$ macrostate in order to discuss equally well the behaviour in any other macrostate, such as the $(N, P, T)$ macrostate appropriate to our piece of copper.

Towards the end of the book (Chapters 12 and 13, in particular), we shall return to the question as to how to set up methods of statistical physics which correspond to other macrostates.

## 1.2   MICROSTATES

Let us now consider the mechanical microscopic properties of the system of interest, which we are assuming to be an assembly of $N$ identical microscopic particles. For the given $(N, U, V)$ macrostate there are an enormous number of possible '*microstates*'.

The word microstate means the most detailed specification of the assembly that can be imagined. For example, in the classical kinetic theory of gases, the microstate

would need to specify the (vector) position and momentum of each of the $N$ gas particles, a total of $6N$ co-ordinates. (Actually even this is assuming that each particle is a structureless point, with no internal degrees of freedom like rotation, vibration, etc.) Of course, this microstate contains a totally indigestible amount of information, far too much for one to store even one microstate in the largest available computer. But, worse still, the system changes its microstate very rapidly indeed – for instance one mole of a typical gas will change its microstate roughly $10^{32}$ times a second.

Clearly some sort of averaging over microstates is needed. And here is one of those happy occasions where quantum mechanics turns out to be a lot easier than classical mechanics.

The conceptual problem for classical microstates, as outlined above for a gas, is that they are infinite in number. The triumph of Boltzmann in the late 19th century – had he lived to see the full justification of it – and of Gibbs around the turn of the century, was to see how to do the averaging nevertheless. They observed that a system spends equal times in equal volumes of 'phase-space' (a combined position and momentum space; we shall develop these ideas much later in the book, in section 14.4). Hence the volume in phase-space can be used as a statistical weight for microstates within that volume. Splitting the whole of phase-space into small volume elements, therefore, leads to a feasible procedure for averaging over all microstates as required. However, we can nowadays adopt a much simpler approach.

In quantum mechanics a microstate by definition is *a quantum state of the whole assembly*. It can be described by a single $N$-particle wave function, containing all the information possible about the state of the system. The point to appreciate is that quantum states are discrete in principle. Hence although the macrostate $(N, U, V)$ has an enormous number of possible microstates consistent with it, the number is none the less definite and finite. We shall call this number $\Omega$, and it turns out to play a central role in the statistical treatment.

### 1.3   THE AVERAGING POSTULATE

We now come to the assumption which is the whole basis of statistical physics:

>   *All accessible microstates are equally probable.*

This averaging postulate is to be treated as an assumption, but it is of interest to observe that it is nevertheless a reasonable one. Two types of supporting argument can be produced.

The first argument is to talk about time-averages. Making any physical measurement (say, of the pressure of a gas on the wall of its container) takes a non-zero time; and in the time of the measurement the system will have passed through a *very* large number of microstates. In fact this is why we get a reproducible value of $P$; observable fluctuations are small over the appropriate time scale. Hence it is reasonable that we should be averaging effectively over all accessible microstates. The qualification

'accessible' is included to allow for the possibility of metastability. There can be situations in which groups of microstates are not in fact accessed in the time scale of the measurement, so that there is in effect another constant of the motion, besides $N, U$ and $V$; only a subset of the total number $\Omega$ of microstates should then be averaged. We shall return to this point in later chapters, but will assume for the present that all $\Omega$ microstates are readily accessible from each other. Hence the time-average argument indicates that averaging over all microstates is necessary. The necessity to average *equally* over all of them is not so obvious, rather it is assumed. (In passing one can note that for a gas this point relates to the even coverage of classical phase-space as mentioned above, in that quantum states are evenly dispersed through phase-space; for example see Chapter 4.)

The second type of supporting argument is to treat the postulate as a 'confession of ignorance', a common stratagem in quantum mechanics. Since we do not in fact know which one of the $\Omega$ microstates the system is in at the time of interest, we simply average equally over all possibilities, i.e. over all microstates. This is often called an 'ensemble' average, in that one can visualize it as replicating the measurement in a whole set of identical systems and then averaging over the whole set (or ensemble).

One can note that the equality of ensemble and time averages implies a particular kind of uniformity in a thermodynamic system. To give an allied social example, consider the insurer's problem. He wishes to charge a fair (sic) premium for life insurance. Thus he requires an expectation of life for those currently alive, but he cannot get this by following them with a stop-watch until they die. Rather, he can look at biographical records in the mortuary in order to determine an expectation of life (for the wrong sample) and hope for uniformity.

## 1.4   DISTRIBUTIONS

In attempting to average over all $\Omega$ microstates we still have a formidable problem. A typical system (e.g. a mole of gas) is an assembly of $N = 10^{24}$ particles. That is a large enough number, but the number $\Omega$ of microstates is of order $N^N$, an astronomically large number. We must confess that knowledge of the system at the microstate level is too detailed for us to handle, and therefore we should restrict our curiosity merely to a *distribution* specification, defined below.

A distribution involves assigning individual (private) energies to each of the $N$ particles. This is only sensible (or indeed possible) for an assembly of *weakly interacting particles*. The reason is that we shall wish to express the total internal energy $U$ of the assembly as the sum of the individual energies of the $N$ particles

$$U = \sum_{l=1}^{N} \varepsilon(l) \tag{1.1}$$

where $\varepsilon(l)$ is the energy of the $l$th particle. Any such expression implies that the interaction energies between particles are much smaller than these (self) energies $\varepsilon$.

Actually any thermodynamic system must have some interaction between its particles, otherwise it would never reach equilibrium. The requirement rather is for the interaction to be small enough for (1.1) to be valid, hence 'weakly interacting' rather than 'non-interacting' particles.

Of course this restriction of approach is extremely limiting, although less so than one might first suspect. Clearly, since the restriction is also one of the assumptions of simple kinetic theory, our treatment will be useful for perfect gases. However, it means that for a real fluid having strong interactions between molecules, i.e. an imperfect gas or a liquid, the method cannot be applied. We shall return briefly to this point in Chapter 14, but a full treatment of interacting particles is well outside the scope of this book. At first sight it might seem that a description of solids is also outside this framework, since interactions between atoms are obviously strong in a solid. However, we shall see that many of the thermal properties of solids are nevertheless to be understood from a model based on an assembly of $N$ weakly interacting particles, when one recognizes that these particles need not be the atoms, but other appropriate entities. For example the particles can be phonons for a discussion of lattice vibrations (Chapter 9); localized spins for a discussion of magnetic properties (Chapters 2 and 11); or conduction electrons for a description of metals and semiconductors (Chapter 8).

A *distribution* then relates to the energies of a single particle. For each microstate of the assembly of $N$ identical weakly interacting particles, each particle is in an identifiable one-particle state. In the distribution specification, intermediate in detail between the macrostate and a microstate, we choose not to investigate *which* particles are in which states, but only to specify the total *number* of particles in the states.

We shall use two alternative definitions of a distribution.

*Definition 1 – Distribution in states*   This is a set of numbers $(n_1, n_2, \ldots, n_j, \ldots)$ where the typical distribution number $n_j$ is defined as the number of particles in state $j$, which has energy $\varepsilon_j$. Often, but not always, this distribution will be an infinite set; the label $j$ must run over all the possible states for one particle. A useful shorthand for the whole set of distribution numbers $(n_1, n_2, \ldots, n_j, \ldots)$ is simply $\{n_j\}$.

The above definition is the one we shall adopt until we specifically discuss gases (Chapter 4 onwards), at which stage an alternative, and somewhat less detailed, definition becomes useful.

*Definition 2 – Distribution in levels*   This is a set of numbers $(n_1, n_2, \ldots, n_i, \ldots)$ for which the typical number $n_i$ is now defined as the number of particles in level $i$, which has energy $\varepsilon_i$ and degeneracy $g_i$, the degeneracy being defined as the number of states belonging to that level. The shorthand $\{n_i\}$ will be adopted for this distribution.

It is worth pointing out that the definition to be adopted is a matter of one's choice. The first definition is the more detailed, and is perfectly capable of handling the case of degenerate levels – degeneracy simply means that not all the $\varepsilon_j$s are different. We shall reserve the label $j$ for the states description and the label $i$ for the levels

description; it is arguable that the *n* symbols should also be differentiated, but we shall not do this.

*Specifications – an example*    Before proceeding with physics, an all too familiar example helps to clarify the difference between the three types of specification of a system, the macrostate, the distribution, and the microstate.

The example concerns the marks of a class of students. The macrostate specification is that the class of 51 students had an average mark of 55%. (No detail at all, but that's thermodynamics.) The microstate is quite unambiguous and clear; it will specify the name of each of the 51 individuals and his/her mark. (Full detail, nowhere to hide!) The definition of the distribution, as above, is to some extent a matter of choice. But a typical distribution would give the number of students achieving marks in each decade, a total of 10 distribution numbers. (Again all identity of individuals is lost, but more statistical detail is retained than in the macrostate.)

## 1.5    THE STATISTICAL METHOD IN OUTLINE

The object of the exercise is now to use the fundamental averaging assumption about microstates (section 1.3) to discover the particular distribution $\{n_j\}$ (section 1.4) which best describes the thermal equilibrium properties of the system.

We are considering an isolated system consisting of a fixed number $N$ of the identical weakly interacting particles contained in a fixed volume $V$ and with a fixed internal energy $U$. There are essentially four steps towards the statistical description of this macrostate which we discuss in turn:

  I.  solve the one-particle problem;
 II.  enumerate possible distributions;
III.  count the microstates corresponding to each distribution;
IV.  find the average distribution.

### 1.5.1    The one-particle problem

This is a purely mechanical problem, and since it involves only one particle it is a soluble problem for many cases of interest. The solution gives the states of a particle which we label by $j$ (= 0, 1, 2, …). The corresponding energies are $\varepsilon_j$. We should note that these energies depend on $V$ (for a gas) or on $V/N$ the volume per particle (for a solid).

### 1.5.2    Possible distributions

The possible sets of distribution numbers $\{n_j\}$ can now be simply written down (given appropriate patience, because usually there will be very many possibilities). However, we give this relatively straightforward task a section of its own, in order to stress that

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