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**an introduction to**  
**STATISTICAL**  
**PHYSICS**

W.G.V. Rosser



# AN INTRODUCTION TO STATISTICAL PHYSICS

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## Author's Preface

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This book is based on a course given by the author to Honours Physics and Combined Honours students in their second year course at Exeter University. Nowadays, solid state physics and related topics form an important part of the third year honours course at British Universities. This means that students should preferably do an introductory course on statistical physics in their second year. At this stage the students are already familiar with Newtonian mechanics, and may have done a course on classical equilibrium thermodynamics, but they will probably only just have started their first comprehensive course on quantum mechanics. Clearly with this restricted background, in the initial stages, a second year course on statistical physics requires a far more simplified approach than can be adopted in a third year course. The author has tried to write the book at the level the average second year student can understand. To achieve this, the first presentation of new material is by means of simple numerical examples. All the mathematical steps are given in full. The basic principles of statistical physics are illustrated by simple numerical examples in Chapter 2. The reader can always return to these numerical examples, if he has any difficulties with the basic formulae used in later chapters. From Chapter 3 onwards the subject is developed axiomatically from three main postulates, namely (i) the existence of discrete quantum states, whose energies are the energy eigenvalues of the appropriate Schrödinger  $N$  particle equation; (ii) the principle of equal *a priori* probabilities, according to which, at thermal equilibrium, all the accessible microstates of a closed isolated system are equally probable; (iii) the law of conservation of energy. These axioms are applied to the case of two systems separated by a partition and surrounded by adiabatic walls so that they make up a closed isolated system. (This corresponds to the microcanonical ensemble.) The Boltzmann distribution (canonical ensemble) and the grand canonical distribution are developed later as special cases. For the benefit of more advanced readers, extra topics are discussed in sections marked with a star (\*). These sections can be omitted in a first reading. The treatment is generally far more concise in

these sections. Some of these sections, for example Chapter 7\*, are designed to make the more advanced reader really think about the subject. Other starred sections are meant as an introduction to more advanced text books. Whenever appropriate, references are given for more advanced reading.

The book has three main aims:

*Aim 1:* To interpret the laws of classical equilibrium thermodynamics in terms of statistical mechanics. This is done mainly in Chapter 3. An interpretation of heat, work and cycles in terms of statistical mechanics is given later in Chapter 7 for the benefit of advanced readers. Ideally, the students should have done an introductory course on classical equilibrium thermodynamics. However, a review of the basic principles of classical equilibrium thermodynamics is given in Chapter 1 in a form suitable for comparison later with the approach to thermodynamics based on statistical mechanics. After covering the basic principles from both points of view, students who have not done an introductory course on classical equilibrium thermodynamics, should be able to follow the application of these principles to practical thermodynamic examples in any of the standard texts on thermodynamics.

*Aim 2:* To develop the Boltzmann distribution in Chapter 4, and the approach to thermodynamics based on the partition function in Chapter 5. The properties of the Helmholtz free energy  $F$  and the Gibbs free energy  $G$  are developed and interpreted in terms of both classical equilibrium thermodynamics and statistical mechanics in Chapter 6.

*Aim 3:* The application of statistical mechanics to quantum phenomena. Planck's radiation law is developed in Chapter 9. This is followed in Chapter 10 by a discussion of the Einstein and Debye theories of heat capacities, leading up to the concept of a phonon. In Chapter 11, the grand canonical distribution is developed and used to derive the Fermi–Dirac and Bose–Einstein distribution functions. Some introductory applications of the Fermi–Dirac and Bose–Einstein distributions are given in Chapter 12.

The author has consulted many text books during the development of the course on which this book is based. He wishes to acknowledge a particular debt to *Statistical Physics* by F. Reif and *Thermal Physics* by C. Kittel, which were used originally as the main course texts. The early influence of *Basic Concepts of Physics* by C. W. Sherwin will be apparent in Chapter 2. I would like to thank Mrs M. Madden and Mrs M. Cornish for typing the manuscript. Finally, I would like to acknowledge my debt to the students at Exeter University, whose questions and enthusiasm made the giving of the course, on which this book is based, such a pleasure.

W. G. V. ROSSER

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## Chapter 1

# A Review of Classical Equilibrium Thermodynamics

---

### 1.1 INTRODUCTION

This Chapter gives a brief review of the main principles of classical equilibrium thermodynamics, presented in a form convenient for comparison later in Chapters 2 and 3 with the microscopic approach to thermodynamics based on statistical mechanics. This Chapter should serve as a refresher course for readers already familiar with classical thermodynamics. Probably the best approach for readers, who have not yet done a full course on classical thermodynamics, is to move on fairly quickly to the microscopic approach presented in Chapters 2 and 3. They can then follow the axiomatic approach to classical thermodynamics given by Callen [1]. Alternatively, having developed the basic principles of thermodynamics in this book, they can read about the practical applications of thermodynamics using a text book which follows the traditional approach to classical thermodynamics, for example, Adkins [2], Pippard [3], Sears and Salinger [4], and Zemansky [5]. As another alternative, they could go on to read a book in which the microscopic and the macroscopic approaches to thermodynamics are combined, as for example in Reif [6]. A reader wanting to do supplementary reading for this Chapter, is referred to any of the standard textbooks on classical thermodynamics such as Adkins [2], Pippard [3], Sears and Salinger [4] and Zemansky [5].

### 1.2 THERMODYNAMIC SYSTEMS

Classical equilibrium thermodynamics developed, mainly in the Nineteenth Century, as a series of laws relating the macroscopic thermodynamic state variables of a system, such as pressure and volume. This was before the development of detailed atomic models in the Twentieth Century. In the practical applications of thermodynamics, by a system we mean that portion of the matter of the universe which is bounded by a

closed surface, as shown in Figure 1.1(a). The rest of the universe forms the surroundings of the system. The boundaries of the system are not necessarily fixed. For example, if a gas expands, the volume of the gas increases and the boundary of the gas system changes. [An example, is shown later in Figure 1.2(a)]. If changes are made to the surroundings of a system, after a period of time the macroscopic thermodynamic variables of a homogeneous system reach new **constant values**. The system is then said to be in a state of internal thermodynamic equilibrium.

As the general case of thermodynamics, it will be convenient to consider the idealised example of two subsystems, labelled 1 and 2, making up a composite closed system, as shown for example in Figures 1.1(b) and 1.1(c). The two subsystems are surrounded by rigid **adiabatic** walls. (An adiabatic wall is a wall which does not conduct heat, whereas a **diathermic** wall allows heat to flow through it). If the outer walls in Figure 1.1(b) are

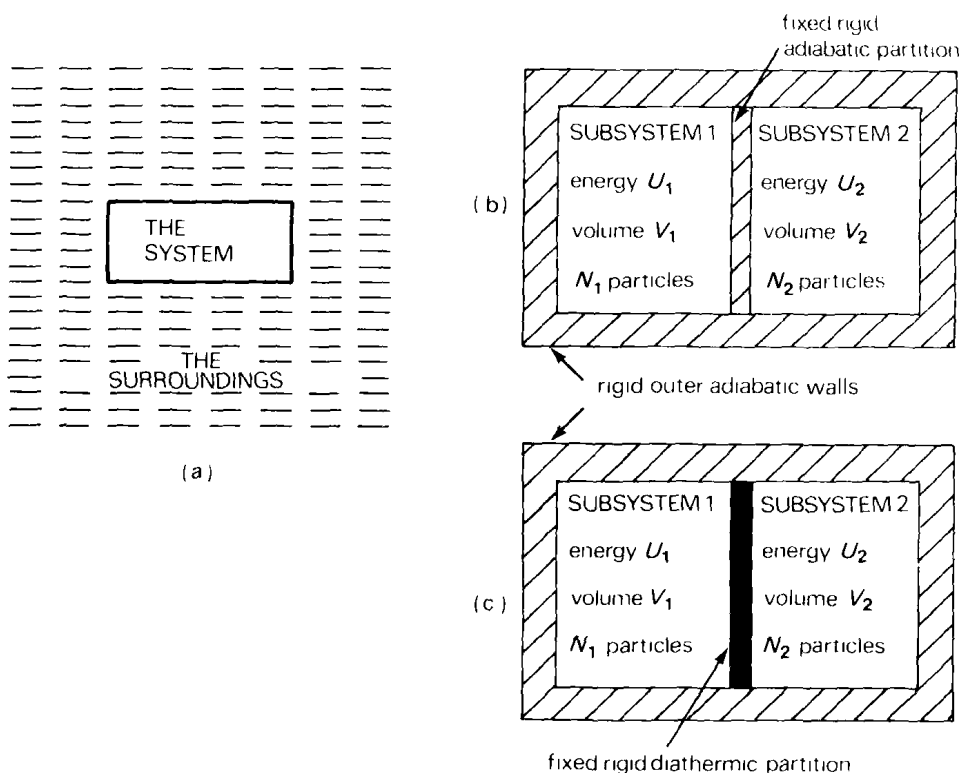


Figure 1.1—(a) Example of a system in thermal equilibrium with its surroundings. (b) An idealised example of two subsystems separated by a fixed rigid adiabatic partition. The two subsystems are inside rigid, outer adiabatic walls and form a closed system of fixed total energy, fixed total volume and fixed total number of particles. (c) The partition in this case is a fixed rigid diathermic partition.



rigid, the total volume ( $V_1 + V_2$ ) of the subsystems does not change. The total energy ( $U_1 + U_2$ ) and the total number of particles ( $N_1 + N_2$ ) in Figure 1.1(b) are also constant. The composite system made up from subsystem 1 plus subsystem 2 is a **closed system**, that is an isolated system of fixed total energy, fixed total volume and a fixed total number of particles.

Subsystems 1 and 2 in Figure 1.1(b) are separated by a partition. If the partition is a fixed, solid, rigid, adiabatic partition, it is an internal constraint of the composite system which prevents the exchange of heat between subsystems 1 and 2. The partition also prevents changes in the volumes of subsystems 1 and 2 and the exchange of particles between the two subsystems. If the partition is a fixed, solid, rigid, diathermic partition, as shown in Figure 1.1(c), heat can flow from one subsystem to the other, but the partition is still an internal constraint of the composite system, preventing changes in the volumes of the subsystems and the exchange of particles between the subsystems.

If the diathermic partition in Figure 1.1(c) is free to move, the volumes of the subsystems can change and one subsystem can do mechanical work on the other. If there are holes in the partition, the subsystems can exchange particles.

To correspond with Figure 1.1(a), we can treat subsystem 1 in Figures 1.1(b) and 1.1(c) as the surroundings and subsystem 2 as the system. As a special case, we can assume that, in Figure 1.1(c), subsystem 1 is very much bigger than subsystem 2, so that subsystem 1 acts as a heat reservoir for subsystem 2. (A heat reservoir is a system whose heat capacity is so very much bigger than the heat capacity of the system in thermal contact with it, that heat flow from or to the heat reservoir does not change the temperature of the heat reservoir significantly.)

### 1.3 MACROSCOPIC AND MICROSCOPIC PHYSICS

**There is no need in classical equilibrium thermodynamics to make any assumptions about atomic structure.** The laws of thermodynamics were developed before the development of detailed atomic models in the Twentieth Century. The laws of thermodynamics lead to general relations *between* thermodynamic variables, enabling us to predict the value of one thermodynamic variable from the values of other thermodynamic variables. The laws of thermodynamics cannot predict the actual magnitudes of individual quantities directly from an atomic model. Our aim in Chapter 3 will be to interpret the laws of classical thermodynamics using a microscopic theory. Statistical mechanics can also be used to predict the values of individual macroscopic quantities. This approach will be developed from Chapter 4 onwards.

Macroscopic variables, such as pressure and volume, can be appreci-

ated directly by our senses. Our sense of sight enables us to visualise, qualitatively, macroscopic changes in volume. Our sense of touch responds to changes in pressure. Atomic theory goes beyond the realm of direct perception. An important quantity relating microscopic and macroscopic quantities is Avogadro's constant  $N_A$ , which is equal to the number of  $^{12}\text{C}$  atoms in 0.012 kilogramme of the isotope  $^{12}\text{C}$ . Avogadro's constant was first determined accurately by Perrin. (One of his methods is outlined in Problem 4.12). The experimental value of Avogadro's constant  $N_A$  is  $(6.022\,5 \pm 0.000\,3) \times 10^{23} \text{ mol}^{-1}$ . A **mole** of any substance is the amount of the substance which contains as many elementary units as there are  $^{12}\text{C}$  atoms in 0.012 kilogramme of  $^{12}\text{C}$ . The elementary unit must be specified and may be an atom, a molecule, an ion, an electron etc., or a group of such entities. For example, a mole of electrons consists of  $6.022\,5 \times 10^{23}$  electrons.

Avogadro's constant is an extremely large number (see Problem 1.1). The unaided eye can resolve about ten lines per millimetre at a distance of 25 cm, and should just about see a cube of side 0.1 mm and volume  $10^{-12} \text{ m}^3$  held at a distance of 25 cm. X-ray analysis has shown that the separation of the atoms in a solid is typically of the order of  $10^{-10} \text{ m}$ , so that each atom should occupy a volume of the order of  $10^{-30} \text{ m}^3$ . Thus a cube of side 0.1 mm made from a solid would contain of the order of  $10^{18}$  atoms, which is a *very* large number. As a typical example of a *small* macroscopic system, we shall therefore take a system of  $10^{18}$  atoms, corresponding to the smallest cube the unaided eye could see.

To illustrate a typical relation between a microscopic and a macroscopic quantity, consider the definition of mass density as the mass per unit volume. Though the diameter of an atom is typically of the order of  $10^{-10} \text{ m}$ , most of the mass of each atom is in the atomic nucleus, which has a diameter of the order of  $10^{-14} \text{ m}$ . On the atomic (microscopic) scale there are enormous fluctuations in mass density in distances of the order of  $10^{-10} \text{ m}$ . The macroscopic mass density can be defined as

$$\rho = \Delta m / \Delta V \quad (1.1)$$

where  $\Delta m$  is the total mass in a volume element  $\Delta V$ , which is large on the atomic scale but small on the laboratory scale. For example, a cube of side  $0.1 \mu\text{m}$  of a solid would contain about  $10^9$  atoms. The fluctuations in mass density average out in such a volume element, which is still small on the laboratory scale. Hence in a macroscopic theory, the mass density, defined by equation (1.1), can be treated as a smooth continuous function of position.

For purposes of discussion, assume that the system in Figure 1.1(a) is a gas. The **macrostate** of the system can be specified by any three of the macroscopic variables  $p$ ,  $V$ ,  $T$  and  $n$ , where  $p$  is the pressure,  $V$  is the