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The Classical Ideal Gas

The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics of such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results.

J. Willard Gibbs

The purpose of Part I of this book is to provide an intuitive understanding of the entropy, based on calculations for a simple model. The model chosen is the classical ideal gas, for which the entropy can be calculated explicitly and completely without any approximations or hidden assumptions.

The treatment is entirely in terms of the theory of classical mechanics. No quantum mechanical concepts are used. All the ideas will follow directly from the work of Ludwig Boltzmann (1844–1906), and especially his 1877 paper on the Second Law of Thermodynamics. We will use more modern mathematical methods than he did to derive the entropy of the classical ideal gas, but we will make no assumptions with which he was not familiar.

In Chapters 7 and 8 the formal expression for the entropy will be extended to classical systems with interacting particles. Although the expression we obtain can rarely be evaluated exactly, the formal structure will be sufficient to provide a basis for the development of thermodynamics in Part II. The same formal structure will also lead to more powerful methods of calculation for statistical mechanics in Parts III and IV.

2.1 Ideal Gas

What distinguishes an ‘ideal’ gas from a ‘real’ gas is the absence of interactions between the particles. Although an ideal gas might seem to be an unrealistic model, its properties are experimentally accessible by studying real gases at low densities. Since even the molecules in the air you are breathing are separated by an average distance of about ten times their diameter, nearly ideal gases are easy to find.

The most important feature that is missing from a classical ideal gas is that it does not exhibit any phase transitions. Other than that, its properties are qualitatively the same

as those of real gases, which makes it valuable for developing intuition about statistical mechanics and thermodynamics.

The great advantage of the ideal gas model is that all of its properties can be calculated exactly, and nothing is obscured by mathematical complexity.

2.2 Phase Space of a Classical Gas

Our model of a classical gas consists of N particles contained in some specified volume. Each particle has a well-defined position and momentum. The positions of all particles can be represented as a point in configuration space—an abstract $3N$ -dimensional space, with axes for every coordinate of every particle. These coordinates can be given in various forms:

$$\begin{aligned} q &= \{\vec{r}_i | i = 1, \dots, N\} \\ &= \{x_i, y_i, z_i | i = 1, \dots, N\} \\ &= \{q_j | j = 1, \dots, 3N\}. \end{aligned} \quad (2.1)$$

The momenta of all particles can be represented as a point in momentum space—an abstract $3N$ -dimensional space, with axes for every component of the momentum of every particle

$$\begin{aligned} p &= \{\vec{p}_i | i = 1, \dots, N\} \\ &= \{p_{x,i}, p_{y,i}, p_{z,i} | i = 1, \dots, N\} \\ &= \{p_j | j = 1, \dots, 3N\}. \end{aligned} \quad (2.2)$$

The kinetic energy of the i -th particle is given by the usual expression, $|\vec{p}_i|^2/2m$, and the total kinetic energy is just the sum of the kinetic energies of all particles,

$$E = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}. \quad (2.3)$$

The complete microscopic state of the system can be described by a point in phase space—an abstract $6N$ -dimensional space with axes for every coordinate and every momentum component for all N particles. Phase space is the union of configuration space and momentum space, $\{p, q\}$:

$$\{p, q\} = \{q_j, p_j | j = 1, \dots, 3N\}. \quad (2.4)$$

Since, by definition, there are no interactions between the particles in an ideal gas, the potential energy of the system is zero.

2.3 Distinguishability

Particles will be regarded as distinguishable, in keeping with classical concepts. To be specific, particles are distinguishable when the exchange of two particles results in a different microscopic state. In classical mechanics, this is equivalent to saying that every point in phase space represents a different microscopic state. Distinguishability does not necessarily mean that the particles have different properties; classically, particles were always regarded as distinguishable because their trajectories could, at least in a thought experiment, be followed and the identity of individual particles determined.

On the other hand, it will be important to remember that experiments on macroscopic systems are always assumed to have limited resolution. In both statistical mechanics and thermodynamics, we are concerned with measurements that do not have the sensitivity to resolve the positions or identities of individual atoms.

2.4 Probability Theory

Because of the importance of probability theory in statistical mechanics, two chapters are devoted to the topic. The chapters discuss the basic principles of the probability theory of discrete random variables (Chapter 3) and continuous random variables (Chapter 5).

The mathematical treatment of probability theory has been separated from the physical application for several reasons: (1) it provides an easy reference for the mathematics, (2) it makes the derivation of the entropy more compact, and (3) it is unobtrusive for those readers who are already entirely familiar with probability theory.

If the reader is already familiar with probability theory, Chapters 3 and 5 might be skipped. However, since the methods for the transformation of random variables presented differ from those usually found in mathematics textbooks, these chapters might still be of some interest. It should be noted that we will need the transformation methods using Dirac delta functions, which are rarely found in mathematical texts on probability theory.

The chapters on probability theory are placed just before the chapters in which the material is first needed to calculate contributions to the entropy. Chapter 3 provides the methods needed to calculate the contributions of the positions in Chapter 4, and Chapter 5 provides the methods required to calculate the contributions of the momenta in Chapter 6.

To apply probability theory to the calculation of the properties of the classical ideal gas—or any other model, for that matter—we will have to make assumptions about the probability distribution of the positions and momenta of 10^{20} or more particles. Our basic strategy will be to make the simplest assumptions consistent with what we know about the system and then calculate the consequences.

Another way of describing our strategy is that we are making a virtue of our ignorance of the microscopic states and assume that everything we don't know is equally likely. How this plays out in practice is the subject of the rest of the book.

2.5 Boltzmann's Definition of the Entropy

In 1877, after a few less successful attempts, Boltzmann defined the entropy in terms of the probability of a macroscopic state. His explanation of the Second Law of Thermodynamics was that isolated systems naturally develop from less probable macroscopic states to more probable macroscopic states. Although Boltzmann's earlier efforts to prove this with his famous H-theorem were problematic and highly controversial, his fundamental insight is essentially correct.

In his 1877 paper, Boltzmann also specified that the entropy should be defined in terms of a composite system; that is, a system composed of two or more subsystems with some sort of constraint between them. An example of such a composite system would be a volume of gas divided into two smaller volumes (or subsystems) by a partition. The partition acts as a constraint by restricting the number of particles in each subsystem to be constant. The removal of the partition would then allow the system to develop from a less probable macroscopic state to a more probable macroscopic state for the distribution of particle positions. The final state, after the composite system had come to equilibrium, would correspond to the most probable macroscopic state. According to the Second Law of Thermodynamics, the thermodynamic entropy should also be maximized in the equilibrium state. The comparison of these two properties of the equilibrium state led Boltzmann to associate the entropy with the probability of a macroscopic state, or more precisely with the logarithm of the probability.

In the following chapters, we will make a direct application of Boltzmann's definition to the calculation of the entropy of the classical ideal gas, to within additive and multiplicative constants that we will determine later.

2.6 $S = k \log W$

Boltzmann's achievement has been honored with the inscription of the equation $S = k \log W$ on his tombstone. The symbol S denotes the entropy. The symbol W denotes the German word *Wahrscheinlichkeit*, which means 'probability'. The natural logarithm is intended, although 'log' is written instead of the more modern 'ln'. Curiously enough, Boltzmann never wrote this equation. It does reflect his ideas, except for the important use of composite systems in his definition. The equation was first written in this form by the German physicist Max Planck (1858–1947) in 1900. The constant k , also written as k_B , is known as the Boltzmann constant.

The symbol W has often been misinterpreted to mean a volume in phase space, which has caused a considerable amount of trouble. This misinterpretation is so common that many scientists are under the impression that Boltzmann defined the entropy as the logarithm of a volume in phase space. Going back to the original meaning of W and Boltzmann's 1877 definition (with composite systems) eliminates much of the confusion about the statistical interpretation of entropy.

The main differences between Boltzmann's treatment of entropy and the one in this book lie in the use of modern mathematical methods and the explicit treatment of the dependence of the entropy on the number of particles.

2.7 Independence of Positions and Momenta

In the derivation of the properties of the classical ideal gas, we will assume that the positions and momenta of the particles are independent. We will present a more formal definition of independence in the Chapter 3, but the idea is that knowing the position of a particle tells us nothing about its momentum, and knowing its momentum tells us nothing about its position. As demonstrated at the beginning of Chapter 4, the independence of the positions and momenta means that their contributions to the total entropy can be calculated separately and simply added to produce the final answer.

2.8 Road Map for Part I

The analysis of the entropy in Part I has been divided into chapters to make it easier to keep track of the different aspects of the derivation.

The concepts and equations of discrete probability theory are developed in Chapter 3, just before they are needed in Chapter 4 to calculate the contributions of the positions to the entropy.

Probability theory for continuous random variables is discussed in Chapter 5, just before its application to the calculation of the contributions of the momenta to the entropy in Chapter 6.

Chapter 7 generalizes the entropy to systems with interacting particles.

Chapter 8 completes the foundations of classical statistical mechanics by relating the partial derivatives of the entropy to the temperature, pressure, and chemical potential.

The following flowchart is intended to illustrate the organization of Part I. The derivation of the entropy of the classical ideal gas follows the arrows down the right-hand side of the flowchart.

Flow chart for Part I

