

Cambridge University Press

978-0-521-86557-9 - An Introduction to Thermodynamics and Statistical Mechanics: Second Edition

Keith Stowe

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Part I

Setting the scene

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Chapter 1

Introduction

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Imagine you could shrink into the atomic world. On this small scale, motion is violent and chaotic. Atoms shake and dance wildly, and each carries an electron cloud that is a blur of motion. By contrast, the behavior of a very large number of atoms, such as a baseball or planet, is quite sedate. Their positions, motions, and properties change continuously yet predictably. How can the behavior of macroscopic systems be so predictable if their microscopic constituents are so unruly? Shouldn't there be some connection between the two?

Indeed, the behaviors of the individual microscopic elements are reflected in the properties of the system as a whole. In this course, we will learn how to make the translation, either way, between microscopic behaviors and macroscopic properties.

A The translation between microscopic and macroscopic behavior

A.1 The statistical tools

If you guess whether a flipped coin will land heads or tails, you have a 50% chance of being wrong. But for a very large number of flipped coins, you may safely

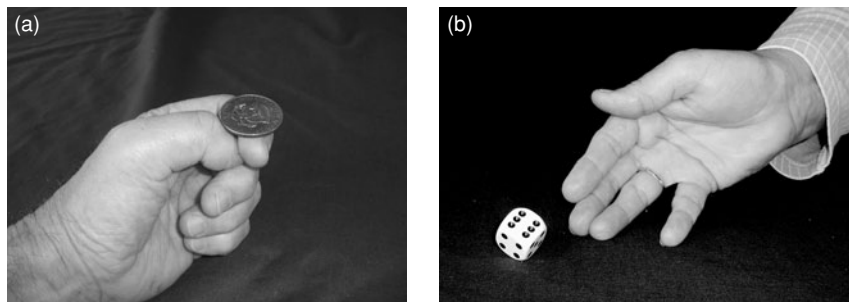


Figure 1.1 (a) If you know the probabilities for one single coin flip then you can predict the heads–tails distribution for a large number of them. Conversely, by observing the heads–tails distribution for a large number of flipped coins, you can infer the probabilities for any one of them. (b) What is the probability that a rolled dice will land with six dots up? If a large number of dice were rolled, roughly what fraction of them would land with six dots up?

assume that nearly half will land heads. Even though the individual elements are unruly, the behavior of a large system is predictable (Figure 1.1).

Your prediction could go the other way, too. From the behavior of the entire system, you might predict probabilities for the individual elements. For example, if you find that one sixth of a large number of rolled dice show sixes (i.e., six dots up), you can correctly infer that the probability for any one die to show a six is $1/6$ (Figure 1.1b). When a system is composed of a large number of identical elements, you can use the observed behavior of an individual element to predict the properties of the whole system, or conversely, you can use the observed properties of the entire system to deduce the probable behaviors of the individual elements.

The study of this two-way translation between the behavior of the individual elements and the properties of the system as a whole is called statistical mechanics. One of the goals of this book is to give you the tools for making this translation, in either direction, for whatever system you wish.

A.2 Thermodynamics

The industrial revolution and the attendant proliferation in the use of engines gave a huge impetus to the study of thermodynamics, a name that obviously reflects the early interest in turning heat into motion. The study now encompasses all forms of work and energy and includes probing the relationships among system parameters, such as how pressure influences temperature, how energy is converted from one form to another, etc.

Considerable early progress was made with little or no knowledge of the atomic nature of matter. Now that we understand matter's elementary constituents better, the tools of thermodynamics and statistical mechanics help us improve our understanding of matter and macroscopic systems at a more fundamental level.

Summary of Section A

If a system is composed of many identical elements, the probable behaviors of an individual element may be used to predict the properties of the system as a whole or, conversely, the properties of the system as a whole may be used to infer the probable behaviors of an individual element. The study of the statistical techniques used to make this two-way translation between the microscopic and macroscopic behaviors of physical systems is called statistical mechanics. The study of interrelationships among macroscopic properties is called thermodynamics. Using statistical tools, we can relate the properties of a macroscopic system to the behaviors of its individual elements, and in this way obtain a better understanding of both.

B Quantum effects

When a large number of coins are flipped, it is easy to predict that nearly half will land heads up. With a little mathematical sophistication, you might even be able to calculate typical fluctuations or probabilities for various possible outcomes. You could do the same for a system of many rolled dice.

Like coins and dice, the microscopic constituents of physical systems also have only certain discrete states available to them, and we can analyze their behaviors with the same tools that we use for systems of coins or dice. We now describe a few of these important “quantized” properties, because we will be using them as examples in this course. You may wish to refer back to them when you arrive at the appropriate point later in the book.

B.1 Electrical charge

For reasons we do not yet understand, nature has provided electrical charge in fundamental units of 1.6×10^{-19} coulombs, a unit that we identify by e :

$$e = 1.602 \times 10^{-19} \text{ C}.$$

We sometimes use collisions to study the small-scale structure of subatomic particles. No matter how powerful the collision or how many tiny fragments are

produced, the charge of each is always found to be an integral number of units of the fundamental charge, e .¹

B.2 Wave nature of particles

In the nineteenth century it was thought that energy could go from one point to another by either of two distinct processes: the transport of matter or the propagation of waves. Until the 1860s, we thought waves could only propagate through matter. Then the work of James Clerk Maxwell (1831–79) demonstrated that electromagnetic radiation was also a type of wave, with oscillations in electric and magnetic fields rather than in matter. These waves traveled at extremely high speeds and through empty space. Experiments with appropriate diffraction gratings showed that electromagnetic radiation displays the same diffractive behavior as waves that travel in material media, such as sound or ocean waves.

Then in the early twentieth century, experiments began to blur the distinction between the two forms of energy transport. The photoelectric effect and Compton scattering demonstrated that electromagnetic “waves” could behave like “particles.” And other experiments showed that “particles” could behave like “waves:” when directed onto appropriate diffraction gratings, beams of electrons or other subatomic particles yielded diffraction patterns, just as waves do.

The wavelength λ for these particle–waves was found to be inversely proportional to the particle’s momentum p ; it is governed by the same equation used for electromagnetic waves in the photoelectric effect and Compton scattering,

$$\lambda = \frac{h}{p} \quad (h = 6.626 \times 10^{-34} \text{ J s}). \tag{1.1}$$

Equivalently, we can write a particle’s momentum in terms of its wave number, $k = 2\pi/\lambda$.

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \quad (\hbar = h/2\pi = 1.055 \times 10^{-34} \text{ J s}). \tag{1.2}$$

The constant of proportionality, $\hbar$, is Planck’s constant, and when divided by 2π it is called “ $\hbar$ -bar.”

We do not know why particles behave as waves any more than we know why electrical charge comes in fundamental units e . But they do, and we can set up differential “wave equations” to describe any system of particles we like. The solutions to these equations are called “wave functions,” and they give us the probabilities for various behaviors of the system. In the next few pages we describe some of the important consequences.

¹ For quarks the fundamental unit would be $e/3$. But they bind together to form the observed elementary particles (protons, neutrons, mesons, etc.) only in ways such that the total electrical charge is in units of e .

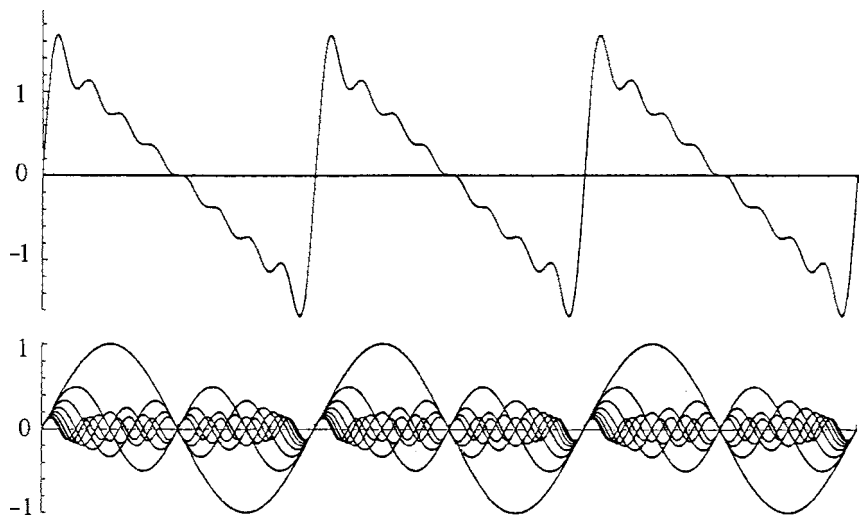


Figure 1.2 The superposition of the sine waves below yields the sawtooth wave above.

B.3 Uncertainty principle

Any function of the variable x on $(-\infty, \infty)$ can be written as a superposition of sine wave components of various wavelengths (Figure 1.2). These sine wave components may be either of the form $\sin kx$ and $\cos kx$, or e^{ikx} , and the technique used to determine the contributions of each component to any function, $f(x)$, is called Fourier analysis. In mathematical terms, any function $f(x)$ on $(-\infty, +\infty)$ can be written as

$$f(x) = \int_0^\infty [a(k) \sin kx + b(k) \cos kx] dk$$

or

$$f(x) = \int_{-\infty}^\infty c(k)e^{ikx} dk,$$

where the coefficients $a(k)$, $b(k)$, $c(k)$ are the “amplitudes” of the respective components.

We now investigate the behavior of a particle’s wave function in the x dimension. Although a particle exists in a certain region of space, the sine wave components, e.g., $\sin kx$, extend forever. Consequently, if we are to construct a localized function from the superposition of infinitely long sine waves, the superposition must be such that the various components cancel each other out everywhere except for the appropriate small region (Figure 1.3).

To accomplish this cancellation requires an infinite number of sine wave components, but the bulk of the contributions come from those whose wave numbers k lie within some small region Δk . As we do the Fourier analysis of various functions, we find that the more localized the function is in x , the broader is the characteristic spread in the wave numbers k of the sine wave components.

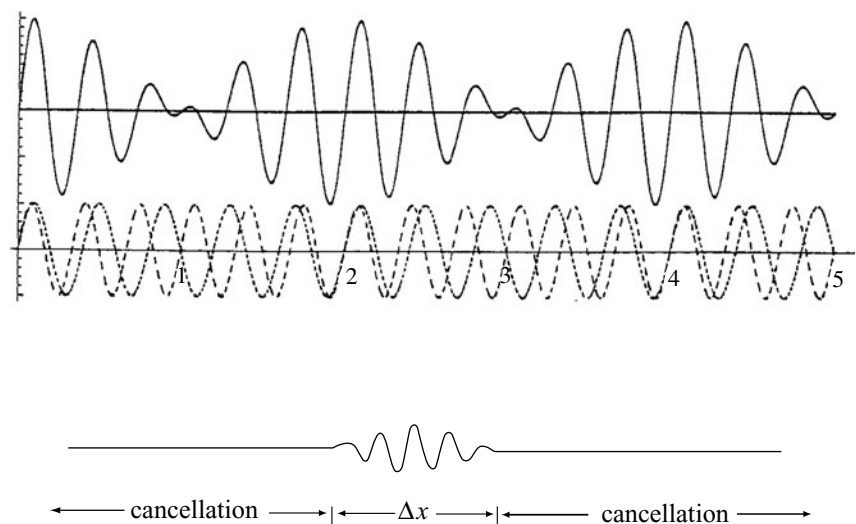


Figure 1.3 (Top) Superposition of two sine waves of nearly the same wavelengths (the broken and the dotted curves), resulting in beats (the solid curve). The closer the two wavelengths, the longer the beats. There is an inverse relationship. (Bottom) In a particle’s wave function, the sine wave components must cancel each other out everywhere except for the appropriate localized region of space, Δx . To make a waveform that does *not* repeat requires the superposition of an infinite number of sine waves, but the same relationship applies: the spread in wavelengths is inversely related to the length of the beat. (The cancellation of the waves farther out requires the inclusion of waves with a *smaller* spread in wavelengths. So the wave numbers of these additional components are closer together and therefore lie within the range Δk of the “primary” wave number.)

In fact, the two are inversely related. If Δx represents the characteristic width of the particle’s wave function and Δk the characteristic spread in the components’ wave numbers, then

$$\Delta x \Delta k = 2\pi.$$

If we multiply both sides by $\hbar$ and use the relationship 1.2 between wave number and momentum for a particle, this becomes the uncertainty principle,

$$\Delta x \Delta p_x = h. \tag{1.3}$$

This surprising result² tells us that because particles behave like waves, they cannot be pinpointed. We cannot know exactly either where they are or where

² The uncertainty principle is written in many closely related forms. Many authors replace the equals sign by $\geq$, to indicate that the actual measurement may be less precise than the mathematics allows. Furthermore, the spread is a matter of probabilities, so its size reflects your confidence level (i.e., 50%, 75%, etc.). We use the conservative value h because it coincides with Nature’s choice for the size of a quantum state, as originally discovered in the study of blackbody radiation.

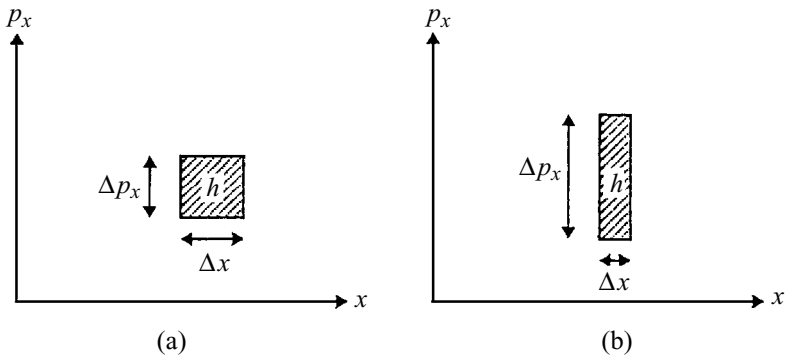


Figure 1.4 (a) According to classical physics, a particle could be located as a point in (x, p_x) space. That is, both its position and momentum could be specified exactly. In modern physics, however, the best we can do is to identify a particle as being somewhere within a box of area $\Delta x \Delta p_x = h$. (b) Because of the wave nature of particles, if we try to specify better the location of a particle in x -space, we lose accuracy in the determination of its momentum p_x . The area $\Delta x \Delta p_x$ of the minimal quantum box does not change.

they are going. If we try to locate a particle’s coordinates in the two-dimensional space (x, p_x) , we will not be able to specify either coordinate exactly. Instead, the best we can do is to say that its coordinates are somewhere within a rectangle of area $\Delta x \Delta p_x = h$ (Figure 1.4a). If we try to specify its position in x better then our uncertainty in p_x will increase, and vice versa; the area of the rectangle $\Delta x \Delta p_x$ remains the same (Figure 1.4b).

B.4 Quantum states and phase space

The position (x, y, z) and momentum (p_x, p_y, p_z) specify the coordinates of a particle in a six-dimensional “phase space.” Although the uncertainty relation 1.3 applies to the two-dimensional phase space (x, p_x) , identical relationships apply in the y and z dimensions. And by converting to angular measure, we get the same uncertainty principle for angular position and angular momentum. Thus we obtain

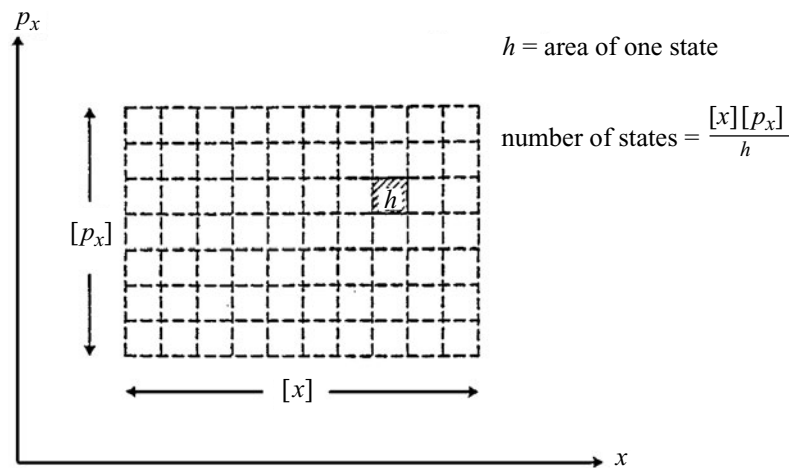
$$\Delta y \Delta p_y = h, \quad \Delta z \Delta p_z = h, \quad \Delta \theta \Delta L = h. \quad (1.3', 1.3'', 1.3''')$$

We can multiply the three relationships 1.3, 1.3', 1.3'' together to get

$$\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z = h^3,$$

which indicates that we cannot identify a particle’s position and momentum coordinates in this six-dimensional phase space precisely. Rather, the best we can do is to say that they lie somewhere within a six-dimensional quantum “box” or “state” of volume $\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z = h^3$.

Figure 1.5 The total number of quantum states accessible to a particle whose momentum is confined to the range $[p_x]$ and whose position is confined to the range $[x]$ is equal to the total accessible area in phase space divided by the area of a single quantum state, $[x][p_x]/h$.



Consider a particle moving in the x dimension whose position and momentum coordinates lie within the ranges $[x]$ and $[p_x]$, respectively (Figure 1.5). The number of different quantum states that are available to this particle is equal to the total accessible area in two-dimensional phase space, $[x][p_x]$, divided by the area of a single quantum state, $\Delta x \Delta p_x = h$. That is,

$$\text{number of accessible states} = \frac{\text{total area}}{\text{area of one state}} = \frac{[x][p_x]}{h}.$$

Extending this to motion in three dimensions we have

$$\text{number of accessible states} = \frac{V_r V_p}{h^3}, \tag{1.4}$$

where V_r and V_p are the accessible volumes in coordinate and momentum space, respectively. In particular, the number of quantum states available in the six-dimensional volume element $d^3r d^3p$ is given by

$$\text{number of accessible states} = \frac{d^3r d^3p}{h^3} = \frac{dx dy dz dp_x dp_y dp_z}{h^3}. \tag{1.5}$$

One important consequence of the relations 1.4 and 1.5 is that the number of quantum states included in any interval of any coordinate is directly proportional to the length of that interval. If ξ represents any of the phase-space coordinates (i.e., the position and momentum coordinates) then

$$\text{number of quantum states in the interval } d\xi \propto d\xi. \tag{1.6}$$

B.5 Density of states

Many calculations require a summation over all states accessible to a particle. Since quantum states normally occupy only a very small region of phase space and are very close together, it is often convenient to replace discrete summation