

PC2135: Thermodynamics and Statistical Physics

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Semester 1, AY2526

Reference: Frederick Reif's Statistical Physics, Berkeley Physics Course, Volume 5

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How to Utilize these Lecture Notes

Our aim in this course is to develop a description of the macroscopic properties of a system via a fundamental understanding of the microscopic behaviour of particles in a *systematic manner*.

As such, at the start of every chapter, the following points will be encapsulated in a little box as such:

- Overview of the chapter
- Intended learning outcome
- Textbook reference
- Flow of chapter

To ensure that you have fully understood the concepts in the lectures, do ensure you are able to achieve the intended learning outcome of the chapter, and can see the link between the contents in the chapter to the overview of the chapter.

These lecture notes were developed to closely follow the reference I utilized, and each chapter will state the particular sections of the book it was based off. I strongly encourage you to read the Reif's book, as the explanations therein will give you a deeper and more nuanced understanding than the lectures can ever give. Learning concepts take time – struggling with words in the textbook is one of the best ways to learn. I will also introduce references of an alternate book (where possible). Different references have different approaches of explaining certain topics. Whilst reading a different reference might cause more confusion at the start, for a more advanced student, these different approaches can be highly enriching. Where possible, I encourage students to look up the supplementary text if they have the capacity.

The main reference this lecture notes are based off will be:

- Reif, Frederick. *Statistical Physics*. Vol. 5 of Berkeley Physics Course, McGraw-Hill, 1967.

The following supplementary references may be useful:

- Schroeder, Daniel V. *An Introduction to Thermal Physics*. Addison-Wesley (Pearson), 1999
- Stowe, Keith. *An Introduction to Thermodynamics and Statistical Mechanics*. 2nd ed., Cambridge University Press, 2007.

Developing a description of the macroscopic properties by drawing links to the microscopic behaviour is no easy feat. One can easily get lost without concrete and explicit examples to anchor the discussion.

Illustration I

As such, it is imperative for students to be aware of the system we are using to illustrate our explanations. The system in question will often be encapsulated in a box like this.

I will draw attention to important definitions and concepts via boxes as below.

Important definitions and concepts will be in these coloured boxes!

Summaries of our long discussions/derivations or worked examples will be encapsulated in a box too!

This box will highlight the summary of discussion and derivations as well as worked examples.

And finally, comments will be in these boxes.

Box 1: Comments

Comments that are potentially tangentially related to the course, or that are related but will be properly introduced and discussed later, will be separated from the main text as such.

I believe strongly that no matter how clear a lecturer is, a student really only learns when they connect the materials on their own and form their own framework of understanding the material. My job is to structure the presentation of the material in a way that it flows smoothly and naturally, and to present this structure in a lucid and comprehensible manner. Your job is to struggle with the concepts and abstract out the main points and connect the ideas in a way that is *your own*. Therefore, part and parcel of using this lecture notes include making your own summary after every chapter/part.

Finally, I do recognize it's no longer "fashionable" nor "trendy" to have content delivered in this form. Shorts, Reels, Snippets and Bite-sized content are all the rage now. Unfortunately, I believe that many nuances get lost in these form of microcontent. Furthermore, students exercise certain skills when processing longer-form content, which are essential competencies tertiary education is meant to cultivate. Therefore, my lectures will be based off these long notes.

Part I

Introduction & Basics

Chapter 1

Macroscopic Systems

Overview:

In attempting to describe a macroscopic system via our understanding of the microscopic characteristics of the system, we build a basic intuition for the concepts of fluctuations, equilibrium and irreversibility. The discussion in this chapter are qualitative in nature. We will be revisiting the concepts explored in this chapter several times throughout this course, sharpening our understanding of said concepts.

Intended Learning Outcomes:

At the end of this chapter, students should be able to:

1. *explain* the fundamental characteristic approach in dealing with macroscopic system.
2. briefly *describe* the concept of equilibrium by considering how a system evolves in time.
3. briefly *describe* the concept of irreversibility.
4. *explain* the meaning of the terms macrostate, microstate and macroscopic parameter with the aid of an example.

Textbook Reference:

Reif: Section 1.1, 1.2, 1.4 and 1.7

Flow of chapter:

1. Fundamental Characteristic Approach
2. Description of Small and Large Systems
 - Illustration I
 - Small systems: Probabilities and Fluctuations
 - Large systems: Probabilities and Fluctuations
3. Approach to Equilibriums and Irreversibility
4. The Equilibrium Scenario

1.1 Fundamental Characteristic Approach

Scientific progress has led us to understand that:

- All matter consists of molecules, built up of atoms. There is overwhelming experimental evidence in support of atomic theory.
- The dynamical behaviour of these atoms and molecules are governed by laws of quantum mechanics, which are well established.
- The electromagnetic forces responsible for the interactions between these atomic particles are very well understood^a.

^aThese are generally the only forces relevant. Gravitational forces on atomic particles are generally negligibly small compared to electromagnetic forces. Nuclear forces are not necessary since we do not concern ourselves with the constituents within the atom.

Hence, in principle, we ought to be able to deduce the properties of any macroscopic system from a knowledge of its microscopic constituents.

The problem: A typical macroscopic system contains about 10^{24} interacting atoms! Hence our knowledge is useless in prediction of any sort unless we develop methods to deal with this complexity. These method should allow us to:

- identify the macroscopic parameters most useful in describing the macroscopic system
- quantitatively predict properties of the system

The solution: We find that the absurdly large number of particles results in statistical methods being remarkably effective to assist us in prediction!

1.2 Description of Small and Large Systems

In this section, we will utilize an example to qualitatively demonstrate how absurdly large numbers mess with our intuition, and how the statistics of large numbers could simplify the macroscopic description of a system.

1.2.1 Set-up & Small Systems

Illustration I

Consider N identical (assumed distinguishable^a) molecules in a container that can be partitioned into two equal parts, with n is the number of molecules in the left half, n' the number of molecules in the right half, such that $n + n' = N$.

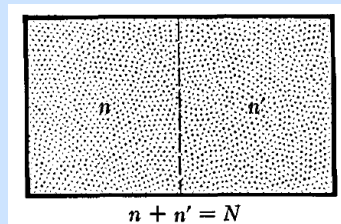


Figure 1.1: A box containing N molecules of ideal gas, subdivided into two equal parts by an imaginary partition, with n molecules on the left and n' molecules on the right

If the gas is sufficiently *dilute*^b, to the point that they are considered *ideal*, they behave like free particles (i.e. no external force exerted on them), only rarely coming into contact with other particles or the wall to interact/collide with them. We will further assume this system is *isolated*, and has been left undisturbed for a very long time.

Ideal: A system that is sufficiently dilute that the interaction between its molecules is almost negligible.

Isolated: A system that does not interact *at all* with any other system.

For the purposes of this illustration, imagine that we can observe the gas molecules without affecting their motion (utilizing a suitable camera, for instance), and we could capture subsequent frames that show the positions of these molecules at regular time intervals τ_0 that are short. These frames can be thought of as a movie strip.

^aIn Physics, the term *identical particles* implies that the particles are *indistinguishable*, a concept that is central to quantum theory. In the classical treatment, particles are never quite indistinguishable as in the quantum sense. We will discuss this concept of identical particles towards the end of this course. This footnote here is just to clarify (especially for those who know more) what I mean by identical when used here – I mean it in the classical sense as different particles that are in principle distinguishable, but are identical – like identical twins!

^bDilute is taken to mean number of molecules per unit volume is small, causing average separation between molecules to be large, and their mutual interactions to be correspondingly small.

Consider the positions of these molecules. A microscopic description or *microstate* of this system would detail the position of every single N molecule within that box. With our knowledge of mechanics, we can indeed predict the location of every single molecule at an arbitrary time t given the initial condition. However, one is rarely interested in this complicated picture.

We would prefer a sufficiently adequate macroscopic description or *macrostate* of the system, which captures sufficient information and for us to make predictions about the system. This macroscopic description would depend on a particular choice *macroscopic parameter*. A macroscopic parameter is a parameter which can be determined by large-scale measurements. Inherent in this parameter is the sensitivity or precision to which our measurements have. For instance, in this example, a macroscopic parameter would be how many particles are in the left half of the box. Depending on the overall number N however, our precision would differ. For $N = 50$, I might consider a ± 5 in my description and a macrostate can be 20-30 particles on the left half of the box. For $N = 10^{24}$ however, a precision of ± 5 would be ridiculous.

Macroscopic parameter: A parameter which can be determined by large-scale measurements and which describes the macroscopic state of a system. Inherent in this choice is the precision which our measurement will have.

Macrostate: State of the system described without attention to the microscopic details, by specifying only the quantities which can be determined by macroscopic measurements (i.e. macroscopic parameter)

Microstate: State of a system described in microscopic detail by the most complete specification, according to the laws of mechanics

Probability and Configurations

If $N = 2$, we would have four different *configurations*, where configuration in this context would be each distinct way in which a molecules can be distributed between the two halves.

Your Illustration: Four different configuration of $N = 2$

Configuration: A particular arrangement that would match a chosen macroscopic constraint (in our illustration, the constraint is the number of molecules N)

With $N = 3$, each molecule will have two possible locations, and the total possible configuration is equal to $2 \times 2 \times 2 = 2^3 = 8$. With $N = 4$, we would have 16 configurations. We list them below. Note that C_n here represents number of configuration with n molecules on left, and P_n represents the probability of having n molecules on the left

1	2	3	4	n	n'	$C(n)$	P_n
L	L	L	L	4	0	1	$1/16$
L	L	L	R	3	1	4	$\frac{4}{16} = \frac{1}{4}$
L	L	R	L				
L	R	L	L				
R	L	L	L				
L	L	R	R	2	2	6	$\frac{6}{16} = \frac{3}{8}$
L	R	L	R				
R	L	L	R				
L	R	R	L				
R	L	R	L				
R	R	L	L				
L	R	R	R	1	3	4	$\frac{4}{16} = \frac{1}{4}$
R	L	R	R				
R	R	L	R				
R	R	R	L				
R	R	R	R	0	4	1	$1/16$

Table 1.1: Possible configurations and probabilities for when $N = 4$

Due to the nature of these molecules that are moving about and colliding with each other, we're never quite sure how many molecules will be in the left half of the box due to *fluctuations*, but we can gauge the chances of expecting n molecules there. The probability of the system being in any one of the configurations about would be $1/16$, as there are 16 possible configurations and we assume *each of them being equally likely* (see Box 1.1). The probability of then having n molecules on the left side is given by the last column in the table.

Box 1.1: Fundamental Postulate of Statistical Mechanics

I have found that although people have no issues each of these 16 configurations being equally likely, they may struggle with what we call the *fundamental postulate of equilibrium statistical mechanics*, or the *postulate of equal a priori probabilities* later on in this course. This fundamental postulate is essentially no different from us assuming equal probability for each of the 16 configurations here. So if you find yourself struggling with this point then, come back here and remind yourself that is really isn't different from this!

Fluctuations

For small $N = 4$, a fluctuation where all 4 molecules are one the left side of the box would occur moderately frequently – about 1 in 16 frames, as computed previously. If we were to plot the relative number of particles on the left side of the box as a function of the frame index, we would obtain a graph like below, for instance.

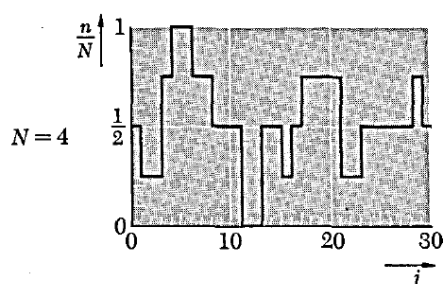


Figure 1.2: Relative number n/N of particles in the left hand half of box as time passes for $N = 4$

1.2.2 Larger Systems

Probability of *one* configuration/situation where $n = N$

As N increases however, we note that the probability of all N molecules being on the left becomes negligibly small, because there's always only one configuration that achieves this.

$$P_N = P_0 = \frac{1}{2^N}$$

Distributions of molecules that are *nonuniform* such that $n \ll N/2$ or $n \gg N/2$ correspond to relatively few configurations. Situations of these kinds that can be obtained in relatively few ways are said to be *nonrandom* or *orderly*^b.

The number of configurations for $n \approx n' \approx N/2$ however increases with N , and the larger the N , the more configurations will correspond to this particular situation. Situations of these kinds that can be obtained in many different ways is said to be *random* or *disordered*. We can (and will) further quantify these statements in the next chapter, but for now an instinctive appreciation of the matter will do.

Random/disordered: A situation that can be achieved in many ways, i.e. a situation that has many configuration corresponding to the particular macroscopic description. (In our illustration the macroscopic description is the number of molecules on the left side of the container, n)

Box 1.2: Putting things into Context

Let us put these things into context. When $N = 4$, we expect 1 in 16 frames in our movie strip to have all 4 molecules on the left. With $N = 80$, we would have $2^{80} \approx 10^{24}$ possible configurations. We would expect 1 in 10^{24} frames to have all 80 molecules on the left. If we took a million pictures every second, you would have to run the film for a time appreciably greater than the age of the universe before we have a reasonable chance of obtaining one frame showing all molecules in the left half of the box^a. Consider now a realistic example of a box having volume 1cm^3 , containing air at atmospheric pressure and room temperature. It would have $N = 2.5 \times 10^{19}$ molecules, which would lead us to approximately $10^{2.5 \times 10^{18}}$.

^aFor context, there are 3.15×10^7 seconds in a year, and the estimated age of the universe is of the order of 10^{10} years.

Probability of a *multiple* configurations/situation of a *range* of possible ns

It is therefore clear that when N is large, large fluctuations are exceedingly rare. However, one might argue that small fluctuations would be similarly common, and that if we group the $N = 50$ into 5 ranges, the probabilities wouldn't differ too significantly the Table 1.1 above. But upon doing the computation (done in tutorials), we note that the actual probabilities work out to be:

No of particles on left, n	$0 \leq n \leq 10$	$10 < n \leq 20$	$20 < n < 30$	$30 \leq n < 40$	$40 \leq n \leq 50$
Probability, P_n	1.19×10^{-5}	0.101	0.797	0.101	1.19×10^{-5}

Table 1.2: Probabilities for 4 different macroscopic scenarios when $N = 50$

These probability values are solely due to the fact that there are more ways to achieve (that is, more configurations that correspond to) the more *random* situation (i.e where n does not vary appreciably from 25).

Fluctuations and Equilibrium

From Table 1.2 above, we can see that for a system where the total number of particles is larger, fluctuations corresponding to an appreciably nonuniform distribution of particles (i.e. $0 \leq n < 10$ in our case, for instance) occurs

^bI find Reif's choice of words here rather confusing. Molecular distribution that are *not uniform* are seen as *not random* or *orderly*. I am sticking with this choice of words to follow Reif, but do take note as it is easy to be confused here.

almost never! Plotting a similar graph of the relative number of molecules on the left hand side of the box may (for instance) result in,

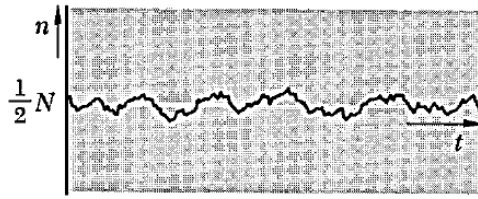


Figure 1.3: Relative number n/N of particles in the left hand half of the box as time passes for large N

A macroscopic description, or macrostate, which does not tend to change much in time is said to be in *equilibrium*. That is, if the description of the macrostate is such that the fluctuations are captured within that description in a way that the macrostate ends up not changing much in time, this macrostate is said to be in equilibrium. For instance, the macrostate where there are 20-30 molecules (out of 50) on the left side of the box is a state that does not change much in time. A system initially with 20-30 molecules on the left of the box will remain in that state a whopping 80% of the time. Whilst this 80% may not be sufficiently high to qualify as equilibrium, one can imagine that a state with 200-300 molecules (out of 500) which has a $P_{200 \leq n < 300} = 0.999991$, would definitely qualify as an equilibrium state. A system initially in that macrostate will remain in that state 99.991% of the time! Recall further that in a realistic situation, N is of the order of 10^{19} !

Equilibrium: A macroscopic state which does not tend to change in time

1.3 Approach to Equilibrium & Irreversibility

Approach to Equilibrium

For the same system with $N = 50$, consider a scenario where $0 \leq n < 10$ at a particular time τ . It matters not how we got to this highly improbable macrostate, all that matters is that the system now is in this state. What can we now say about the probability of each macrostate in the next time step? Clearly Table 1.2 no longer holds as each configuration is no longer equally probable given the initial condition of this system.

In order to preserve this macrostate however, the particles must all move in a particular orderly way. Although we may not want to numerically compute the probability of this, it would align with our understanding that the probability of all the particles moving in such an orderly way would be low. Note further that to *continuously* preserve that macrostate over a course of time is even more unlikely!

As time passes the random motion of the particles will inevitably lead to the situation where this random motion no longer has a discernible effect on the system. By definition, this would be our equilibrium state, since this means the macrostate no longer changes in time. This situation would be the scenario where $n \approx N/2$ (see Fig. 1.4 below). Note that what's at the heart of this behaviour is nothing other than what is known to be the second law of thermodynamics!

Second law of Thermodynamics (Primitive version): If an *isolated* system is in an appreciably non-random situation, it will generally evolve in time so as to approach ultimately it's most random situation where it is in equilibrium.

This is a very primitive version of the second law of thermodynamics. We will sharpen our notion of this second law repeatedly over the course of these lectures to reach our final form, and we will further discuss the other laws in turn.

Irreversibility

Our discussion above demonstrates that when an isolated macroscopic system changes in time, it tends to do so in a very definite direction – from a less random to a more random situation. Now, let the *time-reversed* process be the

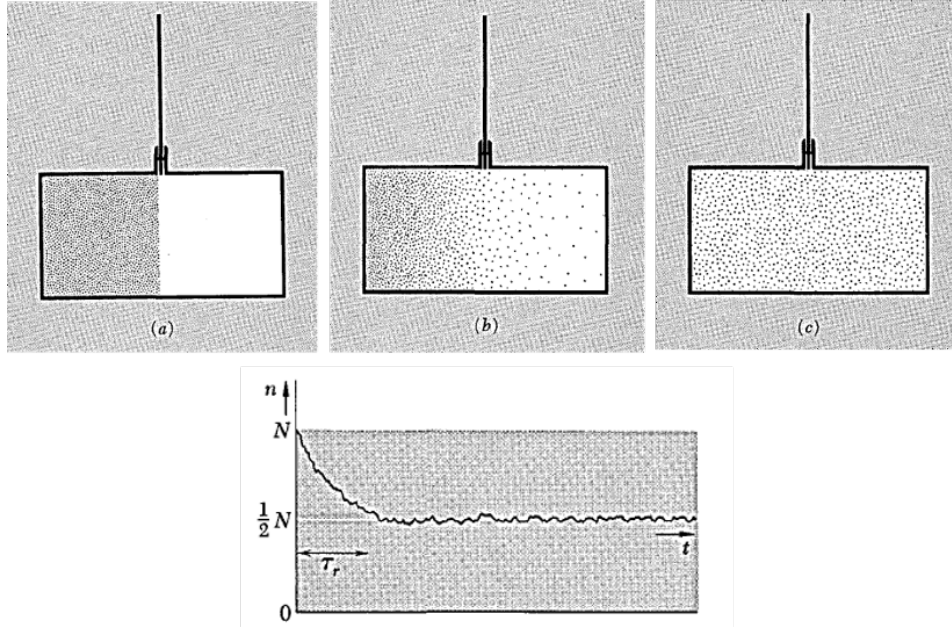


Figure 1.4: Example scenario where initially all n molecules are on the left half of the container due to some external intervention. Probabilistic arguments applied to the velocity of the molecules now dictate that the above course of event is bound to happen. Bottom graph depicts the relative number n/N of particles in the left hand half of the box as time passes given this initial condition.

process that would occur if one imagined the direction of time to be reversed^c. With this conception of a time-reversed process, we are ready to briefly describe an irreversible process.

Irreversible process: An *irreversible* process is a process where the time-reversed version of the process would almost never occur in reality.

It should be clear that there is nothing intrinsic in the law of motion of the particles of a system which gives rise to a preferred direction of time. This preferred direction arises only when one deals with an *isolated* macroscopic system which is somehow *known* to be in a special nonrandom situation initially. Take for instance the scenario where a system arrived at it's orderly state of $n \gg N/2$ due to a very rare spontaneous large fluctuation (left figure below). The forward-time and reversed-time process of that scenario would not be distinguishable unlike the scenario on the right where a specific direction of time is singled out by the knowledge that there was an external interaction prior to it being left undisturbed, as discussed above.

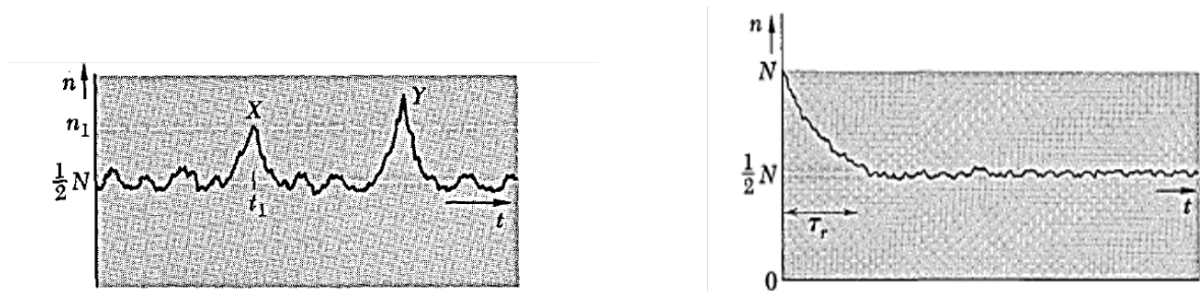


Figure 1.5: Left: No preferred direction of time for the scenario where a system left undisturbed got into a special orderly distribution of $n \gg N/2$ as a result of a very rare spontaneous fluctuation. Right: Preferred direction singled out by knowledge that before being left undisturbed, it was made to interact with some external system.

^cIf we consider taking a video of the system, the time-reversed process would be the video played backwards



Figure 1.6: In the world we're familiar with, we would never expect an *isolated* system to proceed in the time-reversed direction.

Note further that there is a *degree* to the irreversibility in that it becomes more pronounced the more particles there are as the occurrence of an orderly situation is increasingly unlikely with the larger number of particles. The concept of irreversibility would not mean much in the scenario where $N = 4$.

1.4 The Equilibrium Scenario

Just to summarize, in the event it wasn't already clear, a system in equilibrium is particularly simple as the following hold true:

- The macrostate of a system in equilibrium is time-independent, in the sense that the average value of the macroscopic parameter remains constant in time.
- The macrostate of a system in equilibrium is the most random macrostate under the specified condition
- The above point implies that the equilibrium macrostate of the system is independent of its past history (see our discussion in the previous section. It does not matter whether the system originally had a rare large fluctuation or a prior intervention. The final equilibrium state of both scenarios would not be distinguishable).
- We will learn that precisely because the equilibrium macrostate is the most random macrostate, it can be completely specified by very few macroscopic parameters.

Chapter 2

Probability Basics

Overview:

In this chapter we develop a thorough understanding of statistical ensembles and its relationship to the notion of probabilities. We further discuss some elementary relations that probabilities obey and explore some descriptive statistical measures that will allow us to characterize distributions without explicitly specifying the full probability distribution. We will end off the chapter by applying these tools in a sample two-outcome system.

Intended Learning Outcomes:

At the end of this chapter, students should be able to:

1. *explain* the statistical ensemble and its utility.
2. *explain* the concept of equilibrium by considering the statistical ensemble
3. *derive* the elementary relations of probabilities that we utilize from the basic notion/definition of probability.
4. *explain* the significance of two statistical measures we will utilize to describe the distribution, namely the mean and the dispersion/spread (standard deviation) with reference to the statistical ensemble
5. *illustrate* the application of said tools in a sample system with two discrete outcomes.

Textbook References:

Reif: 2.1-2.5

Flow of chapter:

1. Statistical Ensemble
2. Elementary Relations among Probabilities
3. Descriptive Statistical Measures
4. Calculation of Mean Values
 - Illustration II
 - General results
 - Explicit results

Probabilities are indispensable in daily life. We utilize it in games of chance, in insurance business and sampling procedures for polls. They play a fundamental in quantum mechanics and most importantly for us, they will form the basis of our entire discussion of macroscopic systems.

2.1 Statistical Ensembles

Consider a system A , on which we can perform experiments. Often times, the outcome of one single experiment cannot be predicted with certainty for one of two reasons:

- It is intrinsically impossible
- We do not possess sufficient information to permit such a unique prediction

This leads us to a statistical description of our experimental outcomes. Instead of one single system of interest, we now consider an *ensemble* consisting of a very large number \mathcal{N} of “similar” systems^a. By similar, we mean each system satisfies the same conditions known to be satisfied by system A . We then enumerate all possible mutually exclusive outcomes of the experiment, and ask: in what fraction of cases would a particular outcome of an experiment occur. This fraction

$$P_r \equiv \frac{\mathcal{N}_r}{\mathcal{N}} \quad (2.1)$$

is called the probability of occurrence of outcome r . Therefore, although we cannot know the outcome of a single experiment, we now predict the probability of occurrence of a particular outcome.

Box 2.1: The role of information in statistical ensembles

Probability theory is a lot more complex and nuanced than most realize. The interpretation of probability is in fact a matter of serious debate in some circles. There are two main camps (of which, there may be sub-camps): the frequentist interpretation and the Bayesian interpretation. The frequentist interprets probabilities as the frequency of particular outcomes under repeated trials (objective), whereas the Bayesians see probability as a degree of *belief* (subjective).

Most scientific presentation (this included) presents a frequentist version of probabilities. Some do include the nuances of the Bayesian interpretation (this presentation included), by alluding to the information necessary to construct the ensemble to begin with. The probability of the occurrence of any outcome depends crucially on the information available about the system under consideration. This information will affect the *statistical ensemble* chosen, which will then affect the fraction that is our probability.

The example of Reif captures it well. If we’re interested in the probability that a person will be hospitalized at some time between the ages of 28-32, our statistical ensemble will be a large number of people of that age group. However, if we were told that the person is female, our ensemble will now be a large number of *women* of that age group. The resulting fraction may differ significantly as women of that age group may be hospitalized due to reasons men may be exempt from – childbirth, for instance.

When considering a statistical ensemble of systems evolving in time, do note the distinction between

- The behaviour of a single system, say system k as a function of time
- Probabilistic statements about the system at any one time t

Your Illustration: Statistical ensemble

^aIn principle, \mathcal{N} is imagined to be arbitrarily large in the sense of $\mathcal{N} \rightarrow \infty$

With this definition of a statistical ensemble, we are ready to redefine our concept of equilibrium. A statistical ensemble of systems is said to be *time-independent* if the number of its systems exhibiting any particular outcome is the same for every time step. Previously, without the definition of the statistical ensemble, the fluctuation in any one system prohibited us from discussing the outcomes. Although the outcome of any one single system is not well-defined due to fluctuations, the *fraction* of systems exhibiting this outcome over the ensemble always has a well defined value.

Equilibrium: An isolated macroscopic system is said to be in equilibrium if a statistical ensemble of such systems is time-independent.

Note that in the previous chapter, we said that “A system initially with 20-30 molecules on the left side of the box will remain in that state a whooping 80% of the time.” We then proceeded to comment that that percentage may not be sufficiently high to qualify as equilibrium. At that juncture, our language was not sufficiently precise to determine if that was scenario was indeed an equilibrium scenario. Now however, we can. Consider the outcome of 20-30 particles being found on the left. If the fraction of systems displaying that an outcome in one particular time-step is equivalent to the fraction of system displaying that outcome in the next time-step, that would be the equilibrium state!

Box 2.2: Ensemble average versus time average

Note that when the system is in equilibrium, then the ensemble of such a system is *time-independent*. In such a scenario, a large number of *successive* observations on a *single* system will then be equivalent to a large number of *simultaneous* observations on *many* systems. That is the ensemble average at a specific time (averaging over the rows down one single column) is indistinguishable from the time average (averaging over the columns across one single row). This concept of the ensemble average being indistinguishable from the time average, is sometimes known as ergodicity.

2.2 Elementary Relations among Probabilities

These relations we are about to derive are almost self-evident. However going through the process with the concept of the statistical ensemble at the back of your mind would be beneficial.

Set-up

Suppose experiments on system A can lead to any of α mutually exclusive outcomes or events.

- We label each outcome or event by some index $r = 1, 2, 3 \dots \alpha$
- In an ensemble of similar systems, \mathcal{N}_1 of them will exhibit outcome 1, \mathcal{N}_2 of them will exhibit outcome 2, ... and \mathcal{N}_α of them will exhibit outcome α .

Normalization

Probability of either one of two (or more) outcomes

Joint Probabilities

Consider now a scenario where we do two different experiments of the system. We

- label the α possible mutually exclusive outcomes of the first experiment with the index $r = 1, 2, 3, \dots, \alpha$,
- label the β possible mutually exclusive outcomes of the second experiment with the index $s = 1, 2, 3, \dots, \beta$.
- denote \mathcal{N}_{rs} to be the number of systems in an ensemble of \mathcal{N} systems that are characterized by the *joint* occurrence of *both* event r *and* event s .

In summary:

$$\text{Normalization:} \quad \sum_{r=1}^{\alpha} P_r = 1 \quad (2.2)$$

$$\text{Probability of mutually exclusive outcomes } i \text{ or } j: \quad P(r = i \text{ or } r = j) = P_i + P_j \quad (2.3)$$

$$\text{Joint probability distribution } (r, s \text{ statistically independent}): \quad P_{rs} = P_r P_s \quad (2.4)$$

2.3 Descriptive Statistical Measures

In the previous section, we did not care about the value of the outcome, only how frequently it occurred. The reason for this was merely because we were sharpening our concept of probability. In reality, we generally do care about the value of the outcome.

Therefore, consider now a random variable u that can assume α possible distinct values

$$u_1, u_2, u_3, \dots, u_{\alpha}$$

with probability

$$P_1, P_2, P_3, \dots P_\alpha,$$

where we know

$$P_r = \frac{\mathcal{N}_r}{\mathcal{N}}.$$

The most complete statistical description of the random variable u is given by the specifications of probability distribution P_r for all u_r values. However, one can also characterize the distribution of this random variable via other statistical measures. We will discuss the two most fundamental ones in this section.

2.3.1 Mean Value (i.e. Ensemble Average)

We are given a variable u that assumes possible values u_r with respective probability P_r . The mean \bar{u} indicates the central value of u about which the various values of u_r are distributed, while taking the frequency of its occurrence into account.

Definition

Property I: Ensemble average of function of u , $\bar{f}(u)$

Property II: Ensemble average of sum of functions of u , $\overline{f(u) + g(u)}$

Property III: Ensemble average of a constant multiple of a function of u , $\overline{cf(u)}$

Property IV: Ensemble average of the product of the function of two statistically independent variables, $\overline{f(u)g(v)}$

Consider now two different variables u and v , which can assume the following values

$$u_1, u_2, u_3 \dots u_\alpha$$

$$v_1, v_2, v_3 \dots v_\beta$$

In summary: The central value of u about which the various values of u_r are distributed is but the ensemble average value of u , and given by,

$$\bar{u} = \sum_{r=1}^{\alpha} P_r u_r \quad (2.5)$$

The following is true about this average:

$$\bar{f}(u) = \sum_{r=1}^{\alpha} P_r f(u_r) \quad (2.6)$$

$$\overline{f(u) + g(u)} = \bar{f}(u) + \bar{g}(u) \quad (2.7)$$

$$\overline{cf} = c\bar{f}(u) \quad (2.8)$$

$$\overline{f(u)g(v)} = \bar{f}(u)\bar{g}(v) \quad (2.9)$$

Note that Eq. (2.9) only holds in the special case where u and v are statistically independent.

2.3.2 Dispersion

The mean value \bar{u} returns us the central value of u about which the values of u_r are scattered about. However, we don't know anything about *how spread out* this distribution of u_r are. The dispersion is one measure to characterize this spread.

In summary: To measure the spread of u_r about \bar{u} , we consider the standard deviation

$$\Delta u = \left[\overline{(\Delta u)^2} \right]^{1/2} = \left[\sum_{r=1}^{\alpha} P_r (u - \bar{u})^2 \right]^{1/2} \quad (2.10)$$

2.4 Calculation of Mean Values: Spin System Example

A knowledge of the complete probabilities P_r for all values of u_r will give us complete statistical information about the distribution of the values of u_r . However computing the actual values of P_r can prove difficult and time-consuming. Even the simplest case of a two-outcome N particle ideal system is arduous to do by hand (as will be seen in tutorials!).

In this section, we would like to see if any conclusions can be made about the mean values and the spread of these values, without actually specifying the complete underlying probability distribution of the macroscopic system. In particular, we are interested in the following two points:

- Could we link the mean value of the macroscopic parameter to the mean value of the corresponding microscopic property of a singular microscopic system? Could we do the same for the dispersion?
- Could we therefore then determine the mean value of the macroscopic parameter and its associated spread by just specifying the probability distribution of a singular microscopic system?

2.4.1 Set-up

Illustration II

Consider an ideal system^a of N identical (assumed distinguishable) spin- $\frac{1}{2}$, each having associated magnetic moment μ_0 .

For the sake of generality, suppose the spin system is located in an external magnetic field \mathbf{B} . The measurement of the component of the magnetic moment of the spin along a particular direction^b can take only two possible values $+\mu_0$ (parallel to \mathbf{B}) or $-\mu_0$ (anti-parallel to \mathbf{B}). For simplicity, we will denote the first outcome as spin up, the second as spin down.

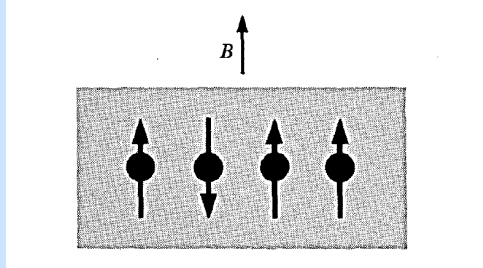


Figure 2.1: A system consisting of $N = 4$ ideal spins $\frac{1}{2}$. Each arrow indicates the direction of the magnetic moment of the spin. The direction of the external magnetic field is denoted by \mathbf{B} .

We denote the probability that a single spin points in the up direction as p , and the probability it points in the down direction as q , such that $p + q = 1$. When $\mathbf{B} = \mathbf{0}$ ^c, there is no preferred direction in space, and therefore

$$p = q = \frac{1}{2}.$$

Let n be the number of magnetic moments pointing up and n' be the number of moments pointing down such that

$$n + n' = N$$

The total magnetic moment M is given by the algebraic sum of the individual magnetic moments over all the N particles

$$M = \mu_1 + \mu_2 \dots + \mu_N$$

^aThe particles might be electrons, atoms with one unpaired electron, or nuclei such as protons.

^bTaken to be the direction of \mathbf{B} here

^cIn the presence of non-zero \mathbf{B} , the magnetic moment will be more likely to point in the direction of the field than against it, $p > q$. For the moment, we will assume the value of p is given. We will learn to compute this value in a later chapter.

2.4.2 Relative Magnitude of Fluctuation

The total magnetic moment M of the system above is the outcome of the experiment that whose distribution we are concerned with. Therefore, in the following, we discuss the mean and dispersion of M where,

$$M = \sum_i^N \mu_i \quad (2.11)$$

Be well aware that the sum over i is over the *particles*, and not over the *outcomes* as the sum over r in the previous sections were.

Mean

Dispersion

In summary: For a general spin system^a

$$\text{Mean :} \quad \overline{M} = N\bar{\mu} \quad (2.12)$$

$$\text{Dispersion/variance :} \quad (\Delta M)^2 = N(\Delta\mu)^2 \quad (2.13)$$

$$\text{Standard Deviation :} \quad \underline{\Delta}M = \sqrt{N}\underline{\Delta}u \quad (2.14)$$

^aNote that although our particular system is a spin- $\frac{1}{2}$ system, the discussion in this subsection so far has not referred explicitly to the underlying probability distribution not the necessity for a two-outcome scenario. Therefore this discussion holds for any generic spin system

Discussion

In particular, note from Eq. (2.12) that the mean of M is proportional to N , the number of particles available, whereas from Eq. (2.14) the standard deviation of M is proportional to \sqrt{N} . Therefore the *relative magnitude* of $\underline{\Delta}M$ compared to \overline{M} *decreases* as N increases:

$$\frac{\underline{\Delta}M}{\overline{M}} = \frac{1}{\sqrt{N}} \frac{\underline{\Delta}\mu}{\bar{\mu}} \quad (2.15)$$

It is hard to fully appreciate the importance of this result right now, but it is crucial to the understanding of the second law down the line. This is basically at the heart of the argument that when N is large, the probability distribution becomes very sharply peaked – because the spread of the distribution, relative to the mean of the distribution, decreases. Note that the spread itself *increases* as can be seen in Eq. (2.14), but the spread *relative* to the mean decreases. Recall further that our course deals with insanely large values of N .

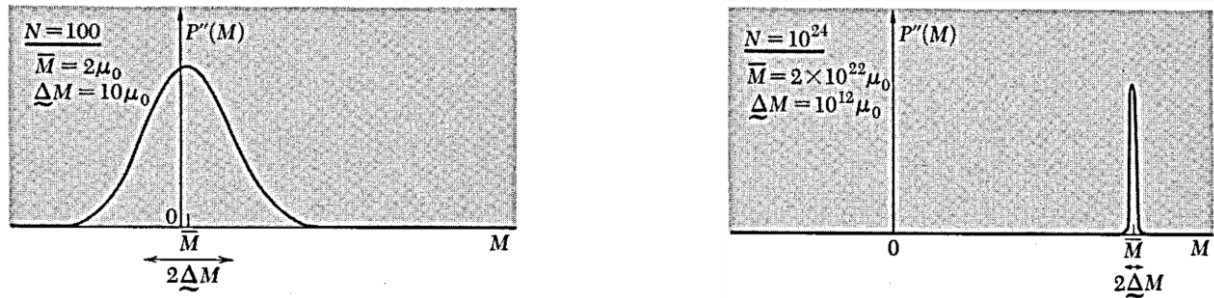


Figure 2.2: Example taken from the textbook that demonstrates how the probability distribution becomes very sharply peaked when $N \sim 10^{24}$

We will come back to this argument many times over the course of these lectures. This is also related to the reason why the values in Table 1.2 are the way they are. Compared to 4 particles, the probability distribution of 50 particles is a lot more sharply peaked! We can (and will) work out those numbers in tutorials, but the numbers alone may not be able to convey the deeper meaning associated with it.

Relative magnitude of fluctuation: The relative magnitude of the standard deviation compared to the mean of a quantity is a good measure of the *relative magnitude of fluctuation* of that quantity. We will find that for most if not all quantities, this ratio scales as per $1/\sqrt{N}$, decreasing with increasing N . In fact, at the values of N that we consider for statistical mechanics ($N \sim 10^{24}$), this relative magnitude of fluctuations are so small that our probability distributions are sharply peaked about the mean value.

2.4.3 Explicit Results for Spin- $\frac{1}{2}$ System

Our particular spin- $\frac{1}{2}$ system is a two-outcome system. Keep in mind the statistical ensemble during this discussion, as it is extremely easy to confuse between the average across the ensemble and the sum across the particles.

Your Illustration: Statistical ensemble of our spin- $\frac{1}{2}$ system

Our aim in this section is to obtain an explicit expression for $\bar{\mu}$ and $\underline{\Delta}u$ for our system of N ideal spin- $\frac{1}{2}$ to insert into Eq. (2.12) and Eq. (2.14). To that end, recall that each spin μ can take only two values:

- μ_0 with probability p , or
- $-\mu_0$ with probability $q = 1 - p$.

In summary: For our spin- $\frac{1}{2}$ system,

$$\text{Mean :} \quad \overline{M} = N(p - q)\mu_0 \quad (2.16)$$

$$\text{Dispersion/variance :} \quad \overline{(\Delta M)^2} = 4Npq\mu_0^2 \quad (2.17)$$

$$\text{Standard Deviation :} \quad \underline{\Delta} M = 2\sqrt{Npq}\mu_0 \quad (2.18)$$

2.4.4 Discussion

We started out this section by introducing the system we would discuss. We then proceeded to link the mean of the macroscopic parameter (total magnetic moment) to mean of the property (magnetic moment) of an individual spin particle. We did the same for the dispersion. Lastly, we obtained the expression of the mean and associated dispersion of the macroscopic parameter by specifying the full probability distribution of the property for the individual spin particle.

Note that the full probability distribution of the *macroscopic* system would be far more difficult to specify! We will see this in our tutorials. As N increases, specifying the full probability distribution of the macroscopic system quickly gets out of hand. However, our discussions here allow us to compute the mean and spread of the macroscopic parameter without requiring the full probability distribution!

Part II

Foray into Statistical Mechanics

Chapter 3

A System of Particles

Overview:

In this chapter we revisit our discussions in Chapter 1 with a more quantitative touch. We will combine the *statistical* considerations in Chapter 2 with our knowledge of the laws of *mechanics* to describe a macroscopic system of particles in a approach known as *statistical mechanics*. At the end of this chapter, we will revisit our notion of irreversibility, suggesting a(nother) primitive version of the second law.

Intended Learning Outcome:

At the end of this chapter, students should be able to:

1. *state* the four generic ingredients needed to describe a system of particles.
2. *illustrate* what constitutes specification of states of a system via some common examples.
3. *construct* the relevant statistical ensemble with the information available.
4. *state* the fundamental postulate upon which the entirety of equilibrium statistical mechanics is built upon and *discuss* its relationship to the concept of equilibrium.
5. *describe* how one would compute various mean values of interest that aids in the description of the system.
6. *elucidate* the necessary steps required to express the dependence of $\Omega(E)$ on E as well as $\ln \Omega(E)$ on f .
7. *explain* the concept of irreversibility with reference to the statistical ensemble.

Reference:

Reif: 3.1-3.6

Flow of Chapter:

1. Basic Formulation
2. Specification of State of the System
 - Illustration III and Illustration IV
3. Statistical Ensemble
4. Statistical Postulates
5. Probability Calculation
6. Number of States Accessible to a Macroscopic System
7. Sharpening our Notion of Irreversibility

Indeed, the generic framework utilized to describe a macroscopic system is similar to that which is used to describe the outcome of our coin flip example we considered (or will consider) in tutorials. The basic aim in this chapter is to distil and articulate this framework from our coin-toss example and apply it to systems we might be interested in describing.

We will deconstruct this into four main ideas. Outlined in the next section are some descriptions of these ideas and how they can be applied to our example of 100 coin-flip of that we covered in tutorial. Each of the following sections after that detail how one would apply these ideas to systems we may be potentially interested in. Let's dive in.

3.1 Basic Formulation

The four ideas in this generic framework of statistical mechanics are:

3.1.1 Specification of the state of the system

We must have a method to specify the microstates of the system before we can proceed to do any computations.

For the coin-toss example, the state of an individual element in the system is specified by which face points up when it lands. The microstates we were concerned with in the tutorial were the exact order of heads and tails in one particular run of 100 coin-flips. This is the most reasonably precise description for this scenario.

Note the qualifier “reasonably precise”: Technically the microstate is meant to be *the* most precise description of the system which would take into account every single atom in all the 100 coins and the precise force exerted by every single atom in the coin-flippers fingers in contact with the coins and... you get the drift (see Section 1.2 for the definition of microstates). When we specify the state of the system in statistical mechanics, we do indeed specify it to this microscopic detail. We weren’t using the term microstates in the most accurate manner in our tutorials.

For the rest of this section, let microstates refer strictly to the complete precise description of the 100 coins and the manner in which they were flipped.

3.1.2 Statistical ensemble

Armed with both the laws of mechanics and a precise knowledge of the particular microstate of our system of interest, we would be able to describe the properties of our system at any arbitrary time to the greatest detail.

In practice, we generally have far too little information (about the precise manner in which the coins are tossed, for instance) to properly utilize the law of mechanics on our system to predict the properties of interest (the result of the coin-flips) precisely. Note that the properties of interest here depend on the chosen *macroscopic parameter*, and can be seen as a *macrostate*, see Section 1.2.

Note that each microstate corresponds *definitively* to *one* macrostate. However, our lack of knowledge about the microstate leads us to describe the macroscopic system in terms of probabilistic concepts. We therefore resort to constructing an ensemble consisting of a very large number of similar systems, subjected to the same macroscopic constraints^a. And we shift our focus from predicting a particular outcome precisely (the order of heads and tails of *this* particular experiment of 100 coin tosses), to predicting instead the *probability* of occurrence of all the possible outcomes (all combinations of different orders of heads and tails of 100 coin tosses).

It must be clear to students that the final aim of this whole endeavour is the prediction of this probability.

3.1.3 Statistical postulates

Now, evidently the ensemble we build is theoretical. We will not employ a coin-flipper to flip coins $100 \times \mathcal{N}$ times. Therefore, we must adopt a *postulate* about the coin’s *a priori*^b behaviour. We postulate that the coin has equal probability of landing on each of its two faces. It is a reasonable postulate, and can be verified by experimental observations.

3.1.4 Probability calculation

With the postulate above, we are ready to compute the probability of occurrences of any particular outcome with reference to our statistical ensemble. For instance, we could be interested in the probability of obtaining at most 3 heads. We will utilize statistical measures like mean and standard deviation of the ensemble to answer whatever questions we’d like to answer.

^aIn this example, it maybe 100 coins and the same coin flipper, for instance. Recall our discussion of the role that information plays in statistical ensembles in Box 2.1. The macroscopic constraint will affect the ensemble we construct.

^b*A priori* (Latin for “from the earlier”) refers to knowledge, reasoning, or assumptions that are independent of experience. It is based on logic, theory, or deduction rather than observation or empirical evidence. [This is from chatGPT, because I couldn’t put accurately into words what *a priori* meant to me].

3.2 Specification of the State of the System

Our aim is to describe a system of particles. The physical laws that govern these particles are the laws of quantum mechanics, and they will form the conceptual basis of our entire statistical mechanics treatment. In this course, quantum mechanical knowledge is assumed insofar as it is necessary to understand the relevant concepts involved^c.

Before we go on, let me clarify that state or quantum state in the paragraphs below generally refer to the state of the *system as a whole*, all N particles of it. Although there are times that we might be discussing the state of the individual particle, but more often than not, we're referring to the state of the entire system.

The essence of a quantum mechanical description^d of an isolated system is as such: The system possesses a set of discrete quantum states, characteristic of the system^e. At any one time, the system can be in any one^f these discrete states. Each of these states is associated with a definite value of its energy, commonly referred to as its *energy level*. There may be several quantum states corresponding to the same energy of the system, and these states are said to be *degenerate*. Every system has a lowest possible energy, and generally there is only one state that corresponds to this state, known as the *ground state*. The states with higher energy levels (in most cases infinitely many of them) are known as *excited states*.

These quantum states are generically specified by specifying some sort of *quantum number*. In order to fully specify a quantum state, one would need to specify the quantum number for each *degree of freedom* of the quantum state. In general the degrees of freedom of a system is the number of parameters of a system that may be varied independently^g. In our context, it's also the number of independent ways one can store energy.

For simplicity, we will label each quantum state with an index r and assume all the possible quantum states can be listed and enumerated in some convenient order, $r = 1, 2, 3, \dots$. Each r here will represent a collection of f quantum numbers.

Specification of state: The microscopic state of a system can be specified by specifying the particular values assumed by the set of f quantum numbers of the system, where f corresponds to the number of degrees of freedom of the system.

We will utilize some examples to clarify these notions.

3.2.1 Ideal system of N spins

This is essentially Illustration II in Section 2.4.1. Before we discuss the ideal N system case, we briefly consider the case of a single spin.

Single Spin in a B field

Consider a single spin- $\frac{1}{2}$ particle with a fixed position and magnetic moment of magnitude μ_0 . The two discrete state this moment could potentially be in with respect to any specified direction is “up” or “down” (i.e. parallel or anti-parallel) to that direction.

Therefore this system has only two quantum states, each of whose quantum number we will denote with σ . A spin up will be denoted as $\sigma = +1$, and a spin down will be denoted as $\sigma = -1$.

In the presence of a **B** field which specifies the direction of physical interest, the energy of the system will be lower when it's aligned parallel to the field. The table below summarizes the quantities of interest.

^cFor instance, it is assumed that students comprehend the concept of energy eigenstates and quantum numbers. It is also assumed that students are familiar with the quantum description of some well-known systems. Familiarity does *not* imply ability to derive said expressions and descriptions. This course will not test the student's ability to solve the Schrödinger equation, although we expect students to know what “solving the Schrödinger equation” means.

^dAt least that we will use.

^eI'm referring here to the energy eigenstates of the system, which are fully specified by the system's Hamiltonian.

^for any combination of

^gQuoted from [wikipedia](#)

r	σ	M	E
1	+1	μ_0	$-\mu_0 B$
2	-1	$-\mu_0$	$+\mu_0 B$

Table 3.1: Quantum states of a single spin- $\frac{1}{2}$ having a magnetic moment μ_0 in a magnetic field \mathbf{B} . σ represents the quantum number associated with each state, M the corresponding magnetic moment and E the corresponding energy of that state.

N Ideal Spin in a \mathbf{B} field

With this basic understanding of a single spin, we are ready to consider a system consisting of N spins.

Illustration III

Consider now a system consisting of N ideal^a spin- $\frac{1}{2}$ particles that are fixed in position. The system is located in an applied \mathbf{B} field.

The orientation of the i -th spin can thus be specified by the quantum number σ_i where +1 denotes that spin pointing up and -1 denotes it pointing down. A particular state of the system can then be specified by specifying each of the N moments.

r	σ_1	σ_2	σ_3	σ_4	M	E
1	+	+	+	+	$4\mu_0$	$-4\mu_0 B$
2	+	+	+	-	$2\mu_0$	$-2\mu_0 B$
3	+	+	-	+		
4	+	-	+	+		
5	-	+	+	+		
6	+	+	-	-	0	0
7	+	-	+	-		
8	-	+	+	-		
9	+	-	-	+		
10	-	+	-	+		
11	-	-	+	+		
12	+	-	-	-	$-2\mu_0$	$2\mu_0 B$
13	-	+	-	-		
14	-	-	+	-		
15	-	-	-	+		
16	-	-	-	-	$-4\mu_0$	$4\mu_0 B$

Table 3.2: Possible configurations and probabilities for when $N = 4$

Note how there is no degeneracy of the ground state. In this example, there is also no degeneracy of the highest possible energy state, but this is not common behaviour, as here we are ignoring the spatial degrees of freedom.

^aIn this system, it amounts to the \mathbf{B} field of one spin being virtually negligible at the position of another spin.

The 16 possible microstates of a $N = 4$ ideal spin- $\frac{1}{2}$ system are enumerated in a convenient order in Table 3.2. This is how one would specify the state of such a system.

3.2.2 Ideal gas of N Particles in a Box

This is similar to Illustration I in Section 1.2.1. Before we discuss the ideal N particles in a 3D box case, we briefly consider firstly a particle in a 1D box, followed by a particle in a 3D box before we move on to N particles in a 3D box.

Particle in a one-dimensional box

Consider a single particle of mass m , confined to a perfectly rigid, one-dimensional box with infinitely high potential walls. The length of the box spans the range $0 \leq x \leq L$. The quantum mechanical description of this particle is given by its wavefunction $\psi(x)$ ^h, which is obtained by solving the Schrödinger equation. The formal solution is:

$$\psi(x) = A \sin \frac{n\pi x}{L}, \quad (3.1)$$

where n can take on any integral values $n = 1, 2, 3, \dots$. Each state has energy

$$E = \frac{\pi^2 \hbar^2}{2mL^2} n^2. \quad (3.2)$$

The quantum number associated with each state is n . We note from Eq. (3.2) that for a box of macroscopic proportions, the separation between the energy levels of successive states is very small due to the value of the reduced Planck's constant, \hbar .

Particle in a three-dimensional box

The generalization to a particle in a three-dimensional box is relatively straightforward. Now a single particle of mass m is confined to the region

$$0 \leq x \leq L_x \qquad 0 \leq y \leq L_y \qquad 0 \leq z \leq L_z$$

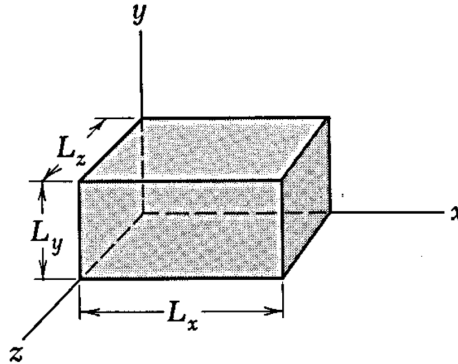


Figure 3.1: A 3D box!

The wavefunction of the particle now is of the form

$$\psi(x) = A \sin \left(\frac{n_x \pi x}{L_x} \right) \left(\frac{n_y \pi y}{L_y} \right) \left(\frac{n_z \pi z}{L_z} \right), \quad (3.3)$$

with each state having the energy

$$E = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (3.4)$$

Any particular quantum state would be designated by a tuple of 3 values (n_x, n_y, n_z) , as a particle in a box has three degrees of freedom.

Ideal gas of N particles in a three-dimensional box

With the two previous discussions out of the way, we can consider the system we are interested in.

^hWhile the wavefunction itself may not have a physical meaning, the amplitude square of the wavefunction $|\psi(x)|^2 dx$ returns the probability of finding the particle between x and $x + dx$.

Illustration IV

Consider now a system of N identical (assumed distinguishable) particles, each of mass m confined within the box of Fig. 3.1. The total energy E of this gas is now just the sum of the energies of the individual particles:

$$E = \epsilon_1 + \epsilon_2 + \dots + \epsilon_N \quad (3.5)$$

where each ϵ_i takes on the expression of Eq. (3.4).

Note that each particle in the box has 3 degrees of freedom, and therefore the whole system has $3N$ degrees of freedom. Therefore each possible quantum state of the entire system can be specified by the values assumed by the $3N$ quantum numbers

$$\{n_{1x}, n_{1y}, n_{1z}; n_{2x}, n_{2y}, n_{2z}; \dots; n_{Nx}, n_{Ny}, n_{Nz}\}. \quad (3.6)$$

Therefore, the state of a system of N molecules of ideal gas in a box can be specified by these set of $3N$ quantum numbers of the system.

This concludes the discussion on specification of states. We have seen how one specifies the state of a system via two example systems.

3.3 Statistical Ensemble

We have discussed the need for the statistical ensemble in 3.1.2. Do refer back if the need for the ensemble is not clear.

In the previous section we were specifying the complete *microscopic* description of the system, which defined the so-called microstate. In the same way, a complete *macroscopic* description of the system will define the so-called macrostate of the system. This description is based on the specification of quantities which can be readily ascertained by *macroscopic* measurements on the ensemble. The information provided from these macroscopic measurements (from which we will build our statistical ensemble, recall Box 2.1) typically fall into two main categories.

Information about the *external parameters* of the system

There will be certain parameters of the system that are macroscopically measurable, which will affect the motion of the particles within the system. We call these the *external parameters* of the system. In our examples above, the \mathbf{B} field and the length of the boxes L_x , L_y and L_z were these external parameters. As can be seen in Table 1.2 and Eq. (3.4), these parameters affect the energy levels of each quantum state. Therefore without a knowledge of these external parameters, we cannot determine the actual energies of individual quantum states.

External parameter: A macroscopically measurable parameter whose value affects the motion of the particles in a system and thus the energies of the possible quantum states of the system.

Information about the *initial preparation* of the system

Conservation laws in mechanics impose certain general restrictions on the subsequent evolution of the particles in the system, depending on the initial parameters of the system. For instance, consider an isolated system originally prepared with some total energy, which we can determine with some finite precision to be $E + \delta E$. The laws of mechanics require that the total energy of an isolated system be conserved such that its total energy must always be between $E + \delta E$. Therefore, the system is constrained to only be in quantum states that have energy values within that range.

We shall call these states that obey the constraints imposed by the initial preparation of the system the *accessible* states. The statistical ensemble selected must be in accordance with the information available about the system, and therefore will comprise of systems all of which are in these accessible state. As an example refer back to Table 3.2, if we know that the total energy of this isolated system of 4 spins is 0, there will be 6 accessible states.

Given a particular *macrostate*, the number of accessible *microstates* of the system is ordinarily very large, for the values of N that are realistic in our discussion ($\sim 10^{23}$).

With these discussions, we can sharpen our concepts of:

Microstate: A particular quantum state of a system. It corresponds to the most detailed possible specification of a system described by quantum mechanics.

Macrostate: A *complete* specification of a system in terms of macroscopically measurable parameters.

Accessible states: Any microstate in which a system can be found without contradicting the macroscopic information available about the system.

3.4 Statistical Postulates

So far, we haven't discussed the time-evolution of our system. For the purposes of this course, we will state without proof that:

- (a) A system in a given microstate will continuously make transitions between the various states accessible to it. See Box 3.1 for a quick overview.
- (b) There is nothing intrinsic in the laws of mechanics that will cause the system to prefer one of the accessible states over any others.

Box 3.1: Time-Evolution in Quantum Mechanics

The matter discussed in this box is not of direct relevance to our course (in the sense that not knowing these will not affect your ability to comprehend the material of this course). However, it's nice to see the connection between the different fields of Physics.

With our knowledge of quantum mechanics, we know that an eigenstate of the Hamiltonian operator (which were the microstates we were describing in the previous sections) evolves in time by only acquiring a phase factor. As a result, the *observable* properties (given by $|\psi|^2$) are supposedly time-independent. We would therefore expect that our state would *not* evolve with time.

However, a state could be in a *superposition* of states, which may potentially allow for transition between states when measured. Furthermore, although we are considering *ideal* systems that are *isolated*, in reality no system is ever truly isolated nor truly ideal. There may be small perturbation of the external field that may cause transition between states, and there may be small interactions that exist between the particles that cause these minute transition between microstates of the specified energy range.

Consider now a system which is *known* at some time to have *equal* probability to be in any one of its accessible statesⁱ. We would therefore from (b) above expect this uniform distribution over the accessible states to remain unchanged in time^j. The probability of finding this system in each one of its accessible state is therefore time-independent!

Your Illustration: Probability distribution is independent of time!

ⁱHow do we know this? It's immaterial. For the moment, we assume that we do know this. This translates to a statistical ensemble with a uniform probability distribution over all its accessible states.

^jThe laws of mechanics can indeed be applied to an *ensemble* of isolated systems to show explicitly that if a system is initially uniformly distributed over all their accessible states, they will remain uniformly distributed over these states forever. This is known as the "Liouville theorem", the proof of which requires knowledge of mechanics beyond the scope of this course.

Recall from Section 1.2 that a system is said to be in equilibrium if its macroscopic state does not change in time. If the probability distribution of the microstates of this system is time-independent, the mean value of every measurable macroscopic parameter of the system would also be time-independent. Therefore, a system that has equal probability to be in any one of its accessible states would be therefore be in equilibrium.

If an isolated system is found with equal probability in each one of its accessible states, it is in equilibrium.

Consider now an isolated system which is *known* at some time to be in some *subset* of states accessible to it. The laws of mechanics impose no restrictions preventing the system from transitioning to one of the other accessible states outside this subset however. Indeed, by virtue of (a) above, we expect transition between accessible states. The net effect of this is analogous repeated shuffling of a deck of cards. If shuffling is kept up long enough, the cards get so mixed up that each card is equally likely to occupy any position in the deck! In the same way, we expect that the system will ultimately become uniformly distributed among all its accessible states.

Your Illustration: Isolated system known to be in a subset of states accessible to it.

From these discussions, we can distil a slightly more refined (though still primitive) version of our second law!

Second law of Thermodynamics (Primitive version II): If an isolated system is not found with equal probability in each one of its accessible states, it is *not* in equilibrium. It then tends to change in time until it attains ultimately the equilibrium situation where it's found with equal probability in each one of its accessible states.

This primitive version of the second law leads us to our fundamental postulate of equilibrium statistical mechanics, also sometimes known as *postulate of equal a priori probabilities*.

Fundamental Postulate: If an isolated system is in equilibrium, it is found with equal probability in each one of its accessible state.

Box 3.2: Interpretation of Probabilities – NOT important for the course

In Bayesian probability, there is the concept of **Principle of Insufficient Reason**, which states: *In the absence of any relevant evidence, agents should distribute their credence ("degree of belief") equally among all the possible outcomes under consideration.* I will leave it to you to discuss the philosophical relevance of this to the postulate of equal *a priori* probabilities.

With these statements *together*, we are essentially claiming that *being in equilibrium* and *having an equal probability of occupying each accessible state* are logically equivalent statements.

Your Illustration: Matters of logic

With this, we can now sharpen our notion of equilibrium.

Equilibrium: An isolated system is said to be in equilibrium if the probability of finding the system in any one of its accessible states is independent of time. (The mean values of all macroscopic parameters of the system are then independent of time)

We started this section by discussing time-evolution of our system. Note that the description of the time-evolution itself is not our main aim. Our main aim was the determination of the fundamental postulate from which the rest of our probability calculations will rest on. Our postulate however, applies only to equilibrium situations.

Evidently the discussions become much more complex when dealing with situations that *do* change in time. In this case (which we shall not deal with much in this course), the only statement that still holds in general is the primitive version of the second law, which makes assertions about the *direction* in which the system tends to change. Note however, that we have not discussed the time taken to attain the equilibrium condition, the *relaxation* time. In some cases, one might still be able to apply the equilibrium arguments to situations that do change in time (see Box 3.3).

Box 3.3: Primitive Notion of Quasi-static Operations

Further into our course, we will start discussing interactions with our otherwise isolated system. In situations where these interactions take place over times *much longer* than the relaxation time, we could, in practice, consider the system in equilibrium at all time.

For instance, consider container of gas with a piston, like below. The relaxation time for this system can be found by pulling the piston back very suddenly and determining how long it takes to attain equilibrium.

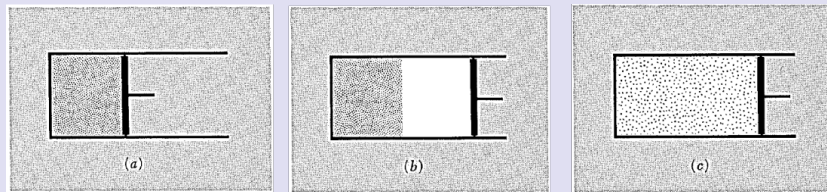


Figure 3.2: Sudden expansion of a gas.

If the system's relaxation time is about 10^{-3} seconds, it would take 10^{-3} seconds for the system to attain equilibrium and for the molecules to be uniformly distributed over the whole volume when the piston is pulled all the way to the right suddenly.

Consider now the operation takes place over 100 seconds. At any instant of time throughout our operation, the molecules in the system would have had sufficient time to be uniformly distributed over the whole volume that is available to it at that time, such that one can imagine the piston to be really stopped at any instant.

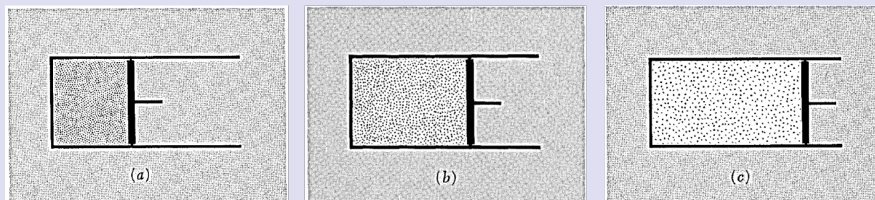


Figure 3.3: Very slow (quasi-static) expansion of a gas.

Your Illustration: Visually applying this step to our 4 spins example with initial preparation $E = 0$

3.5 Probability Calculations

Our task was to give a statistical description of a macroscopic system. In particular, various macroscopic parameters of the system (in our first example system it could be the total magnetic moment) have values that depend on the particular microstate of the system.

We have found a way to predict the probability that the system is found in any given one of its accessible states in the previous section. We should then be able to answer the following question: What is the probability that any parameter of the system assumes any specified value? What is the mean value of such a parameter? What is its standard deviation?

In principle, this calculation is simple. Consider an isolated system in equilibrium and denote by Ω the total number of states accessible to it. For ease of reference, we shall call this Ω the multiplicity. The probability of finding the system in each one of its accessible states, is just $1/\Omega$, from our fundamental postulate.

Suppose now that we're interested in some parameter y of the system, which has a definitive value in each particular state. Enumerating the possible values of y as y_1, y_2, \dots, y_n , we can find the probability P_i that the parameter assumed a particular value y_i by

$$P_i = \frac{\Omega_i}{\Omega} \quad (3.7)$$

where Ω_i is the multiplicity of y_i , or the number of microstates that have the value of y_i for the parameter y . The mean value of y is then just given as

$$\bar{y} \equiv \sum_{i=1}^n P_i y_i = \frac{1}{\Omega} \sum_{i=1}^n \Omega_i y_i \quad (3.8)$$

where the sum is over all possible values of y . The dispersion can also be computed.

Your Illustration: Computing the mean magnetic moment for the 4 spin- $\frac{1}{2}$ example

3.6 Number of States Accessible to a Macroscopic System

In this section, we will proceed to discuss how the application of the basic steps above look in an actual macroscopic system. Applying the steps to a system of 4 spins (done in tutorial) may be straightforward, but enumerating all possibilities keeping count of everything becomes progressively more difficult with more particles. We find, however, that we may bypass this difficult process by making some crude approximations.

Things will start to get a little bit more mathematically involved here. To ensure we don't get lost in the mess, we first summarize the final conclusion. The aim, is to be able to make crude approximations about the number of states $\Omega(E)$ of macroscopic system^k.

^kRecall that multiplicity Ω is essentially the number of accessible states of the system. These accessible states are constrained by the *initial preparation* of the system (see Section 3.3). This is why there is a dependence on E .

At the end of this section, we show the following two points about the number of states $\Omega(E)$, having an energy between E and $E + \delta E$, in a macroscopic system.

- (a) For any ordinary^a system, it is approximately true that

$$\Omega(E) \propto (E - E_0)^f \quad (3.9)$$

where f is the number of degrees of freedom of the system, and E_0 is the ground state energy.

The number of states $\Omega(E)$ accessible to any ordinary macroscopic system is an extremely rapidly increasing function of its energy E , due to the exponent f , which is a fantastically large number.

- (b) For systems that are not close to its ground state (i.e. $E \not\approx E_0$) the logarithm of $\Omega(E)$ is independent of δE and scales like f ,

$$\ln \Omega(E) \sim f \quad (3.10)$$

In this case, $\ln \Omega(E)$, which the number of states having an energy between E and $E + \delta E$ is independent of the width δE of the interval.

^aThere is an exception to this: In the scenario where a system has *finite* number of possible states, and therefore, an upper bound to its possible energy. The scenario where we focus only on the spins as per Illustration III and ignore the kinetic energy of the particle would fall under this exception.

Consider a macroscopic system with given *external parameters* (see Section 3.3 for a refresher) such that its energy levels are determined. The total energy of this system is then denoted as E . For macroscopic systems, the spacing between the energy levels are minuscule¹, and far too small to be measurable. Therefore, to facilitate the counting of states, we will subdivide the energy scale into equal small intervals of fixed magnitude δE . Note that δE is very small on a *macroscopic* scale, but large on a *microscopic* scale. Therefore the interval δE will contain many possible microscopic states of the system. Now, let

$$\Omega(E) \equiv \text{the number of states with energies lying in the interval between } E \text{ and } E + \delta E \quad (3.11)$$

$\Omega(E)$ here depends on δE , although not explicitly included in the notation. Note that $\Omega(E)$ goes to 0 when $\delta(E)$ goes to 0. Therefore expressing $\Omega(E)$ as a Taylor series in powers of δE , and keeping the first order term, we have

$$\Omega(E) = \rho(E)\delta E \quad (3.12)$$

where $\rho(E)$, also called $g(E)$ in some books, is referred to as the *density of states* as it is equal to the number of states per unit energy range at the given energy E . Note that $\rho(E)$ here does *not* depend on the size of δE .

It is possible to determine $\Omega(E)$ if we know the quantity

$$\Phi(E) \equiv \text{the total number of states have energies less than } E \quad (3.13)$$

because the following relationship will hold

$$\Omega(E) = \Phi(E + \delta E) - \Phi(E) = \frac{d\Phi}{dE}\delta E. \quad (3.14)$$

We have obtained $\Omega(E)$, or equivalently $\Phi(E)$ for two worked examples in the gray box in the next page. I recommend referring to that box first before moving on to the more general case.

¹See the comment after Eq. (3.2)

Single particle in a 1 dimensional box

Consider a single particle of mass m free to move in one dimension in a box of length L . From Eq. (3.2), we can obtain

$$E = \frac{\hbar^2 \pi^2}{2m L^2} n^2 \quad \Rightarrow \quad n = \frac{L}{\pi \hbar} (2mE)^{1/2}$$

Since n starts from 1 and increases by one for every state (See Fig. 3.4 below), the number $n - 1$ would be equivalent to the number of states with energy less than E^a .

$$\Phi(E) = n = \frac{L}{\pi \hbar} (2mE)^{1/2}$$

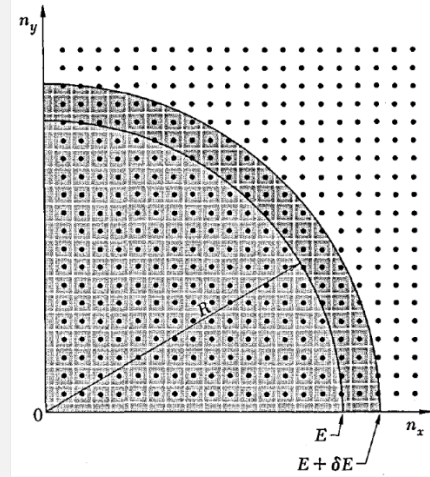
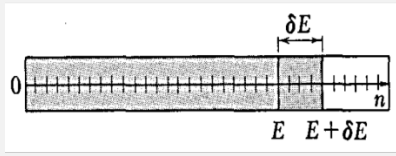


Figure 3.4: *Left:* Points on the line indicate possible values of $n = 1, 2, 3, \dots$ of the quantum number n specifying the state of a single particle in 1D. $\Omega(E)$ represents the number of vertical lines within the δE , and $\Phi(E)$ here represents the number of vertical lines on the left side of E . *Right:* A schematic 2D diagram of the positive octant of the sphere of radius R for the single particle in 3D. The $\Omega(E)$ here represents the number of points within the outer shell of this octant and $\Phi(E)$ represents the number of points in the interior of this octant.

Single particle in a 3 dimensional box

Consider a single particle of mass m free to move in three-dimensional box of length $L_x = L_y = L_z = L$. From Eq. (3.4), we can obtain

$$E = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \quad \Rightarrow \quad n_x^2 + n_y^2 + n_z^2 = \frac{L^2}{\pi \hbar^2} (2mE) \equiv R^2$$

Unlike for the 1D case, for a given value of E , the values of n_x , n_y and n_z which satisfy this equation lie on a sphere of radius R , where

$$R = \frac{L}{\pi \hbar} (2mE)^{1/2}$$

The number $\Phi(E)$ is then equal to the number of unit cubes lying within the positive octant of a sphere (as n_x , n_y and n_z are positive integers). Therefore

$$\Phi(E) = \frac{1}{8} \left(\frac{4}{3} \pi R^3 \right) = \frac{\pi}{6} \left(\frac{L}{\pi \hbar} \right)^3 (2mE)^{3/2}.$$

And thus,

$$\Omega(E) = \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} E^{1/2} \delta E$$

where $V = L^3$ is the volume of the box.

^aBecause n is so large, $n - 1$ is for all practical purposes the same as n .

We will now make a crude order-of-magnitude estimate to find roughly how the number of states $\Omega(E)$, or equivalently $\Phi(E)$ depends on the energy E of the macroscopic system of particles. Recall from our specification of states in Section 3.2 that our system is described by a set of f quantum numbers, where f refers to the number of degrees of freedom of a system.

Let each of these quantum numbers/degrees of freedom contribute an average of ϵ to the total energy E of the system. Therefore, if the lowest possible energy contribution of a degree of freedom is ϵ_0 , then

$$E - E_0 \sim f(\epsilon - \epsilon_0) \quad (3.15)$$

where E_0 represents the lowest possible energy of the system^m.

Let $\varphi(\epsilon)$ be the number of ways one specific degree of freedom/quantum number can achieve energies less than ϵ . When φ is not in the order of unity, that is, when $E \not\approx E_0$ ⁿ, the following is true.

$$\Phi(E) \sim \varphi^f \quad (3.16)$$

Your Illustration: To convince yourself of Eq. (3.16)

Note that φ itself depends on ϵ (and hence, on E) as the possible values that each quantum number can take φ will increase if the average energy contributed per degree of freedom ϵ is higher. For our purposes, we will assume without proof that

$$\varphi(\epsilon) \propto (\epsilon - \epsilon_0) \quad (3.17)$$

Now we will show that

$$\Omega(E) \sim \varphi^{f-1} \delta E \quad (3.18)$$

by starting from Eq. (3.14) and applied the chain rule several times utilizing Eq. (3.15), Eq. (3.16) and Eq. (3.17).

With these, we can therefore make a crude approximation and obtain Eq. (3.9).

$$\Omega(E) \sim \varphi^{f-1} \delta E \propto (\epsilon - \epsilon_0)^{f-1} \propto \left(\frac{E - E_0}{f} \right)^{f-1} \propto (E - E_0)^f$$

^mThe symbol \sim here means “scales like”. It’s sort of like \approx , but this has the idea of two quantities growing or behaving in the same way. In some ways it’s a stronger statement than \approx , which is more of a numerical statement

ⁿWhen φ is of the order of unity, the Φ is the order of unity as well, regardless of how large f is. We already know this intuitively as when the energy approaches the ground state, there is generally only one way to achieve that lowest energy state. See Section 3.2 and the illustrations therein and consider how would one obtain the lowest energy state for the N particle systems.

where the last expression holds because f is generally a *large* (see Box. 3.4) *constant* number. We could also drop the δE from the proportionality since it's a constant value.

Before we end off, let us consider $\ln \Omega$ – the reason for doing this will become apparent in later discussions. Taking the logarithm of Eq. (3.18), we have

$$\ln \Omega \sim f. \quad (3.19)$$

Note that for large numbers, its logarithm is generally utterly negligible compared to itself. For instance, consider $f = 10^{23}$: $\ln f = 55$ and thus $f \gg \ln f$. Therefore, when the system is not close to its ground state^o, we can obtain Eq. (3.10)

Box 3.4: Fantastically Large Numbers

In our discussions of this topic, we will come across three types of numbers.

Small numbers are basically the regular numbers we are familiar with like 8, 23 and 94.

Large numbers are much larger than small numbers, and are generally created by exponentiating large number. In our discussion, the number that comes up often would be 10^{23} . The nice thing about large numbers is that you can *add* a small number to it, without changing it much. For instance,

$$10^{23} + 23 \approx 10^{23}$$

Fantastically large number are numbers that are much larger than large numbers, and refer generally to exponentiation of large numbers. For instance $10^{10^{23}}$. The cool thing about fantastically large numbers is that you can *multiply* them by a large number without changing them much. For instance,

$$10^{10^{23}} \times 10^{23} = 10^{10^{23}+23} \approx 10^{10^{23}}$$

For a better appreciation of the scale of the numbers involved, consider the following table taken from the Stowe reference

grains of sand in Waikiki beach	10^{18}
age of the universe in microseconds	10^{24}
water molecules in Atlantic ocean	10^{46}
atoms in Earth	10^{50}
volume of Universe in cubic microns	10^{97}
states for molecules in a glass of water	$10^{1,000,000,000,000,000,000,000,000,000}$

Table 3.3: Large numbers versus fantastically large numbers

This concludes our discussion on the number of states accessible to a macroscopic system. We have thereby derived a crude approximation of how this number of states depends on its energy. With this number, and our fundamental postulate of thermodynamics, we can crudely describe the probability distribution, and obtain the relevant mean values.

3.7 Sharpening our Notion of Irreversibility

Let us summarize the general structure of what we have developed so far

^oWhen the system is close to its ground state, the equation Eq. (3.16) no longer holds, and therefore the conclusions will not hold any more. See footnote [n](#) for clarification.

- (a) We consider *isolated* systems, known to satisfy certain conditions, described on a macroscopic scale with macroscopic parameter(s) $y(s)$.
- (b) These y constraints the system and restrict the set of allowed *accessible states* of the system, which we denote as $\Omega(y)$.
- (c) The statistical description involves probability statements about an *ensemble* of such systems subjected to the same macroscopic conditions.
- (d) If the system is in *equilibrium*, it will be found to have equal probability to be in any one of its accessible states. If it is *not* in equilibrium, the system will evolve until it has equal probability to be in any one of its accessible states.

Consider an isolated system initially in equilibrium. Suppose now that some of the original constraint of the system was removed. Since the system is now subjected to *fewer* constraints than before, the number of states accessible to the system after the removal of the constraint Ω_f cannot be less than the number of accessible states before the removal, Ω_i . It could, in a special case be equal, but not less. The usual scenario is that $\Omega_f > \Omega_i$. In fact, due to the fantastically large numbers associated with macroscopic systems, we expect Ω_f to generally be much larger than Ω_i .

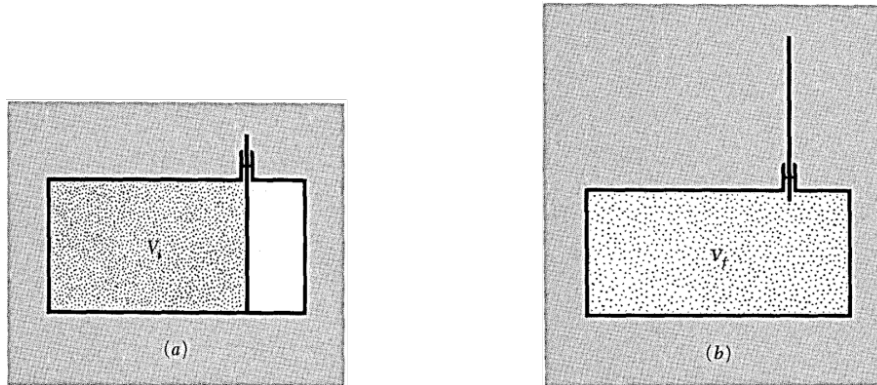


Figure 3.5: An ideal gas confined within a box. *Left*: Initial situation. *Right*: Final situation with fewer constraints

Suppose that the final equilibrium situation has been attained. Note further that the initial situation of the *ensemble* cannot be restored merely by reimposing the former constraint while keeping the system isolated. If we merely consider a single system, one could wait for the occurrence of the right kind of spontaneous fluctuation, and quickly restore the constraint. The probability of this right kind of spontaneous fluctuation occurring however is given by

$$P_i = \frac{\Omega_i}{\Omega_f}. \quad (3.20)$$

For a macroscopic system, $\Omega_f \gg \Omega_i$, as we will see in tutorials.

With this, we can now sharpen our notion of irreversibility.

Irreversible process: A process in which the initial situation of an *ensemble* of *isolated* systems subjected to this process *cannot* be restored by simply reimposing the constraint.

Reversible process: A process in which the initial situation of an *ensemble* of *isolated* systems subjected to this process *can* be restored by simply reimposing the constraint.

A reversible process is merely the converse. Note that a reversible process would refer to the special case where $\Omega_f = \Omega_i$.

With this, we can also sharpen our notion of *randomness* as introduced in Section 1.2.2. The number of accessible states *actually present* in the ensemble of our system can serve as a statistical measure or quantification of randomness. If the every accessible state is equally represented in the ensemble, the system would be in the most random/disordered state it can be. If every member of the statistical ensemble is in one state of out the many accessible states, this is a very ordered/not-random situation.

3.8 The End!

This officially ends our initial foray into statistical mechanics where we describe the basic general formulation of this field as applied to an *isolated* system. In the next chapter we will begin discussing *interaction* between systems, performing the necessary statistical mechanical analysis on them. In those discussions the concepts familiar to thermodynamics will begin to creep in, like the notion of Temperature, Entropy, and the ever famous laws of Thermodynamics.