1 Introduction

Somewhere near the beginning, most introductions to statistical physics contain a sentence along the following lines:

The main aim of statistical mechanics is to derive macroscopic properties of matter from the laws governing the microscopic interactions of the individual particles.

(Thompson, *Mathematical Statistical Mechanics*, p32)

This is in contrast with the older subject of thermodynamics, which proposes some basic laws that govern certain kinds of macroscopic behaviour without probing the microscopic phenomena that give rise to those laws. In principle, one should be able to derive thermodynamics from statistical mechanics. Working out this derivation in detail is an important theoretical task of statistical physics.

The first appearance of a notion of entropy was in the early thermodynamics of the nineteenth century. With the benefit of modern statistical physics, one finds that this appearance of entropy is really a consequence of the same underlying mathematical phenomena as the others we have met in this course.

This lecture: a rough introduction to statistical mechanics based on the theory around entropy that we have already met.

2 Systems

Statistical mechanics analyzes systems that consist of huge numbers of elementary components, usually particles of some kind. The behaviour of these is governed
by the basic laws of either classical or quantum mechanics, depending on the model.

A full introduction to statistical mechanics should start with a discussion of how one isolates a ‘system’, at least conceptually, and describes its relationship to the rest of the universe. That relationship can follow various rules, and these govern the kinds of model that one uses for the system.

Here we omit most of this discussion, and focus instead on some simple examples. As a result, our introduction to statistical mechanics is immediately incomplete. But the examples are quite intuitive, and do illustrate some of the basic phenomena, particularly in relation to entropy.

To get started, imagine an open box $V$ in three dimensional space which contains $n$ classical particles with masses $m_i$ and positions $r_i$. Suppose the particles move in the presence of a potential energy $U$ (such gravitational energy), and that they interact with one another only in pairs which either attract or repel through a force given by a potential energy $\varphi$ that depends on the distance between them (such as electrostatic repulsion). Then, according to Newton’s laws of motion, the positions evolve according to

$$m_i \frac{d^2 r_i}{dt^2} = \text{force on particle } i$$

$$= -\nabla U(r_i) - \sum_{j \neq i} \nabla \varphi(\|r_i - r_j\|). \quad (1)$$

We do not make use of these equations in this lecture: they are placed here only to make the general case for statistical mechanics as a discipline in its own right. For macroscopic systems, we may well have $n \sim 10^{23}$. It is impossible to imagine solving the above equations for motion with that many degrees of freedom. Even if they could be solved, one could never in practice have accurate enough information about the initial conditions of all the particles in the system to derive useful predictions from the solutions.

And yet, many systems in the real world display remarkably smooth and regular behaviour. Some theory should be available to explain this, based on better ideas than just solving the equations of motion.

Statistical mechanics is that theory. When it is successful, it describes the approximate behaviour of certain key macroscopic quantities by finding ways to ignore most of the microscopic detail in the system. The approximations rely on statistical phenomena, so they are good precisely because the system has so many constituents. In a system made up of, say, $10^{20}$ particles, these approximations tend to be fantastically accurate.
3 Thermodynamic equilibrium

A macroscopic description of a system is given in terms of a few real-number parameters. For instance, in simple models of a gas confined to a bounded region, these might be the volume of the region \( V \), the number \( n \) of particles in the gas, and their total energy \( E \). Other systems, such as blocks of magnetic material, require different choices of parameters.

Such a description still leaves enormous freedom as to the microscopic state of the system. For instance, in the example of a gas, we haven’t said how much of the total energy \( E \) is accounted for by the kinetic energies of each of the particles, or the potential energies of their interactions. So, within a given model of a system, there is a big set of possible micro states that are compatible with the chosen macro state.

One of the key ideas of statistical physics is that, to a macroscopic observer, this microscopic variation is essential invisible. Whatever other macroscopic parameter one thinks of, it will take very nearly the same value on most of microstates that are compatible with the given macrostate.

In the first place, this is a fact of experience. If we have two identical mugs on the same table in a room, and they contain identical volumes of coffee at the same temperature, then we usually do not discern any other difference between the mugs of coffee, even though the motions of the individual molecules inside of one are not related to those inside the other in any way.

This indistinguishability of microstates is not supposed to hold for absolutely all possible compatible microstates, only for the overwhelming majority. Indeed, after a system first enters a state described by certain macroscopic parameters, it usually does undergo some further macroscopic changes for a while, before its macroscopic state appears to become still. Microscopically it is still extremely active: particles move around and bounce off of one another all the time. But after a certain relaxation time the system reaches thermodynamic equilibrium, meaning that its macroscopic appearance stays constant.

Moreover, it is precisely that microscopic activity which is responsible for the relaxation of the system into thermodynamic equilibrium: microscopically, the state keeps changing, and if the microscopic dynamics mixes things up sufficiently well, then after a while the initial state of disequilibrium is forgotten and equilibrium is achieved. This, again, is principally a fact of experience. (Early attempts to justify it rigorously rest on the so-called ‘ergodic hypothesis’. We do not explore this here, but historically it is the origin of ‘ergodic theory’ as a subject. We turn to that later in the course.)
This idea of ‘equilibrium’ is really only ever an approximation to the behaviour of the real world; put another way, it is a matter of interpretation. In the hot-mug-of-coffee example, if we care about the behaviour of the coffee over the next few seconds, then maybe we can regard it as being in equilibrium. If we care about the whole of the next hour, then the coffee will noticeably lose heat to the air in the room, and we should not regard equilibrium as being attained until that process is essentially finished.

The convergence to thermodynamic equilibrium is one of the basic observations in the science of thermodynamics. One can describe it without reference to the microscopic state of a system. But in statistical physics, it becomes the first key step towards a new and powerful mathematical formalism.

4 The microcanonical ensemble

Conceptually, it is simplest to model systems that are isolated. This means that the constituent particles have negligible interaction with the rest of the universe.

If a system is isolated, then the values of various physical quantities are constant: this is a consequence of the basic conservation laws that underly all of physics. So a model of an isolated macroscopic system is constrained by its values of certain macroscopic parameters, such as volume, particle-number and energy.

Within such a model, the microscopic basis for the achievement of thermodynamic equilibrium is that, among all possible micro states compatible with those macroscopic parameters, the overwhelming majority ‘look the same’ as regards any other macroscopically measurable quantity.

With this in mind, we reach perhaps the first big idea in statistical mechanics:

For any macroscopic quantity, its behaviour for a system in equilibrium may be predicted very accurately by its average value over all compatible micro states.

Mathematically, the plan is this: rather than tracking the exact trajectory of the system among all possible microstates, we will

1. describe the set of all microstates that are compatible with the given macroscopic parameters;

2. endow that set with a natural probability measure;

3. predict that the values of other macroscopic observables are given by their averages with respect to that probability measure.
If a system is in equilibrium, it shouldn’t matter exactly what microstate it has reached at any given moment: the prediction obtained from step 3 above will be a very accurate guess most of the time. In fact, it turns out to be an extremely accurate guess for an overwhelming fraction of the time.

The choice of the measure in step 2 depends on the model and the description in step 1. In most models there is a natural candidate for the ‘uniform measure on all compatible micro states’, and then this is the measure that we use. In physics it is called the ‘microcanonical ensemble’.

Once one has decided on a sensible microscopic model and on the microcanonical ensemble, it becomes a mathematical problem to decide whether other macroscopic quantities really are roughly constant with high probability. If this is the case, then the real test of our plan above is by agreement with experiment.

5 Simple models of isolated systems

In the model (1) from classical mechanics, the instantaneous state of the system is described by the locations and momenta of all \( n \) particles: that is, by a point in the set
\[
M := V^n \times (\mathbb{R}^3)^n \subseteq \mathbb{R}^{6n}.
\]
These are the initial data needed to evolve the equation (1) (with some additional rules about the nature of collisions with the sides of the box).

For any model, this set of possible states for the whole system is called the state space. Within it, for any real value \( E \), there is an energy surface: in the model above this is the set
\[
\Omega(E) := \left\{ (r_1, \ldots, r_n, p_1, \ldots, p_n) : \right. \\
\frac{1}{2} \sum_{i=1}^{n} m_i \|p_i\|^2 + \sum_{i=1}^{n} U(r_i) + \sum_{i \neq j} \varphi(\|r_i - r_j\|) = E \right\}.
\]
In this model, assuming we have no other natural conserved quantities, the natural choice of microcanonical ensemble is the \((6n - 1)\)-dimensional surface measure on \( \Omega(E) \), normalized to be a probability measure. Of course, we must choose a value of \( E \) for which \( \Omega(E) \) is nonempty, and worry about whether this set is regular enough to carry such a natural surface measure.
We do not analyze such continuous models any further in this lecture. Instead we consider some even simpler discrete models, where the relevant statistical phenomena are more easily uncovered.

So now consider a system which consists of \( n \) generic ‘particles’, each of which has available to it a discrete set \( A = \{a_1, a_2, \ldots \} \) of possible individual states. That set may be finite or countable infinite. The microstate of the whole system is specified by the \( n \) individual states of the particles: that is, by a point in \( A^n \). Such a model with a discrete set of permitted states may seem like a drastic simplification of a mechanical model like (1), but it is actually quite close to the truth according to quantum mechanics.

Each microstate has a total energy. Let us assume further that our particles are **identical** and **non-interacting**. This means there is a fixed energy function \( \Phi_0 : A \rightarrow \mathbb{R} \), called the **Hamiltonian**, such that the total energy of the microstate \( a = (a_1, \ldots, a_n) \) is

\[
\Phi(a) = \sum_{i=1}^{n} \Phi_0(a_i). \tag{2}
\]

(Note: The most common symbol for a Hamiltonian is \( H \); I am using \( \Phi \) instead because I want to keep using \( H \) for Shannon entropy. The choice of \( \Phi \) is quite common among more advanced pure math texts. On the other hand, the standard physical symbol for entropy is \( S \), and I’ll be using \( S \) in a related way shortly, too.)

The cases of finite and infinite \( A \) are slightly different once we enter the more detailed analysis below.

- If \( A \) is finite, then the tools we need are given almost immediately by our previous work on large deviations theory. One useful convention: it will be clear that nothing changes if we adjust the function \( \Phi_0 \) by additive constant, so we may always assume that

\[
\min\{\Phi_0(a) : a \in A\} = 0.
\]

Having done so, any state \( a \) for which \( \Phi_0(a) = 0 \) is called a single-particle **ground state**.

We do make one extra assumption here: that \( \Phi_0 \) takes at least two distinct values. This simply rules out degenerate cases.

- If \( A \) is infinite, then we need to modify those large-deviations results slightly, and this is possible only if we make some (quite reasonable) extra assumptions about \( A \).
Most importantly, if an individual particle has limited energy, then it should not have too many states available to it. The simplest assumption to make is simply that the set \( \{ a \in A : \Phi_0(a) \leq r \} \) is finite for every \( r \in \mathbb{R} \). But it turns out that this is not quite enough for the theory to work correctly. We really need the following more quantitative version of this assumption: for any \( \beta > 0 \), we have
\[
\sum_{a \in A} e^{-\beta \Phi_0(a)} < \infty. \tag{3}
\]
This is equivalent to assuming that the cardinality \( |\{ a \in A : \Phi_0(a) \leq r \}| \) grows subexponentially in \( r \).

Such a precise mathematical assumption may seem surprising so early in the story, but the model below really can degenerate without it. It’s also a very weak assumption, satisfied by all the usual models of basic physical systems.

Having made this assumption, then as in the case of finite \( A \) we may adjust \( \Phi_0 \) by a constant to assume that its minimum value is zero. The term ground state is used here as before.

### 5.1 An important subtlety

This is not an attempt to model a system which is truly ‘non-interacting’. If the particles were isolated and really didn’t interact at all, then they could not exchange energy with one another, and then all of the individual energies \( \Phi_0(a_i) \), \( i = 1, 2, \ldots, n \) would be constant. In this case there would be no mechanism to drive this ‘system’ into equilibrium.

Rather, we are really using \( \Phi(a) \) as an approximation to a Hamiltonian of the form
\[
\sum_{i=1}^{n} \Phi_0(a_i) + \Phi_{\text{interaction}}(a) \quad \text{much smaller, but more complicated} \tag{4}
\]

It is the interactions between particles that serve to mix up their different behaviours and bring the system as a whole towards the ‘typical’ macroscopic behaviour of equilibrium. But the idea in a ‘non-interacting’ model is that, although the presence of \( \Phi_{\text{interaction}}(a) \) is necessary to explain the movement towards equilibrium, it is small enough to be neglected when doing calculations in terms of the microcanonical ensemble.
The microcanonical ensemble in this model is obtained by choosing a value \( E \) and considering the uniform distribution over the set of states for the system whose energy is \( E_n \). In writing it this way, \( E \) is the specific energy of the system: the energy-per-particle. This is natural, because the total energy allowed in the model generally scales like the number of particles.

In fact, we do not ask precisely that the state \( a \) satisfy \( \Phi(a) = E_n \), but only that \( \Phi(a) \) be in a small window around \( E_n \), with an error that is small relative to the total number of particles. This approximation is needed to prevent certain pathologies. But it is also natural if we remember that \( \Phi \) is only an approximation to the true Hamiltonian (4) anyway.

So, in a model of this kind, the microcanonical ensemble at specific energy \( E \) and with error tolerance \( \varepsilon > 0 \) is the uniform distribution on the set

\[
\Omega_n(E, \varepsilon) := \{ a \in A^n : |\Phi(a) - E_n| < \varepsilon n \}.
\]

This should remind you of our various notions of typical sets in information theory. The main new feature of the present setting is that \( A \) can be infinite. But the set \( \Omega_n(E, \varepsilon) \) is finite for any given values of \( E \) and \( \varepsilon \), as a consequence of (3).

### 6 Notes and remarks

Sources for this lecture:

- Our choice of first steps is heavily motivated by [Khi49], although Khinchine stays in the setting of continuous models. See [Ell06, Chapter III] for a much more careful account of an even more special case than the above.

- I like [B06, Chapter 3] for a terse but accessible introduction to statistical physics for applied mathematicians.

Further reading:

- There are many good physics textbooks on statistical physics. I mostly looked at Pathria and Beale’s *Statistical Mechanics*. Classic more advanced books include [Fey98] and [LL80]. But it’s definitely worth shopping around for yourself.

- Several authors have attempted a combined description of information theory and statistical mechanics, but with explanations based on physical ideas rather than mathematics. Two places to start looking into this are [Jay89] and [Bri62].

References


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