Reading assignment

Schroeder, section 2.2.

Recap of lecture 4

- Heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

- The connection:

$$C_P - C_V = TV\frac{\beta^2}{\kappa_T}\,,$$

- Beware of possible quantum freeze-out of degrees of freedom, which alters the heat capacity.
- Enthalpy:

$$H \equiv U + PV\,.$$

- C_P in terms of enthalpy:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

The reason for the success of thermodynamics

I mentioned early on that the observed stability of the macroscopic properties of systems with huge numbers of particles in equilibrium results from the fact that states with those observed properties are overwhelmingly more probable than states with different properties. This provides the essential reason for the success of macroscopic thermodynamics, and entropy, which is closely related to the probability of occurrence of states with particular macroscopic properties, then plays the central role in indicating which macroscopic properties are observed.

Film loop of ping-pong balls on a drum head.

So, we need to develop some machinery for determining the probabilities of macroscopic states. We'll begin by thinking a bit about probability, starting with some combinatorial ideas.

Questions

- Find the number of distinct sequences (order does matter) of n integers in the range $1, \ldots, N$.
- Same as above, but don't allow repetition within a sequence (all elements of each sequence are distinct) [assume $N \geq n$].
- Find the number of distinct *sets* (order doesn't matter) of n integers from the first N integers.

Exercise

How many ways can N numbered balls be divided into 3 groups containing n_1, n_2, and $n_3 = N - (n_1 + n_2)$ balls in each? (Assume that n_1, n_2, and either n_3 or N are given.)

Constituents, microstates, and macrostates

In statistical mechanics we'll consider systems to be composed of some *constituents*, perhaps atoms, molecules, or whatever. This implies some degree of independence of the constituents.

Each constituent will generally be supposed to exist in any of a number of "single-particle" states independently of the others, with the collection of single-particle states of all constituents constituting a *microstate* of the "many-particle" system. The complete set of all possible microstates is called the *microstate space*.

The system as a whole will have certain macroscopic properties that characterize its *macrostate*. Generally, many microstates will have the same macroscopic properties, and we will use that fact in predicting the probability of each of the macrostates. Knowledge of the probabilities of the macrostates is our key goal.

Example

To illustrate these ideas, consider a two-constituent system consisting of a cubic (6-sided) and a tetrahedral (4-sided) die. Each has sides numbered from 1 to the number of its sides.

The “single-particle” (single-die) states of either die can be characterized by the number facing up.

Each microstate of the “many-particle” (two-die) system can be characterized by the pair of numbers characterizing the single-particle states.

We’ll take the (only) macroscopic property of the two-die system to be the sum of the numbers on the dice, so all microstates having the same sum will be lumped together in the same macrostate.

Example

Here is a complete table of the possible microstates:

	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
3	4	5	6	7	8	9
4	5	6	7	8	9	10

And here's a summary of the number Ω of microstates occurring in each macrostate (i.e., having each sum):

Sum:	2	3	4	5	6	7	8	9	10
Ω:	1	2	3	4	4	4	3	2	1

This shows the distribution of the $6 \times 4 = 24$ microstates among the 9 macrostates.

Probability

A useful definition for us is this: imagine generating a long sequence of measurements of the state of some system. For each result, denoted x, determine the ratio

$$\frac{\text{Number of occurrences of } x}{\text{Total number of measurements}}\,.$$

If that ratio converges to a well-defined value in the limit of an infinite number of measurements, that value is called the probability of occurrence $P(x)$.

Probabilities satisfy a couple of important properties:

- If two events are mutually exclusive, the probability of either occurring is the sum of the probabilities of each.
- If two events are independent, that is, the probability of each does not depend on the occurrence of the other, the probability of both occurring is the product of the probabilities of each.

Probability distributions

The set of probabilities for a complete set of (i.e., all possible) events is called a *probability distribution*, and to qualify as such it is necessary that a set of numbers $P(x)$ satisfy

$$0 \leq P(x) \leq 1$$

and

$$\sum_{x \in \Omega} P(x) = 1\,,$$

the latter being the normalization condition. Here x indexes the events of interest, such as occurrences of the microstates or of the macrostates.

Example

In the previous example, to calculate the probability of each macrostate of the two dice, we need the probabilities of each of the microstates. Those, in turn, depend on the probabilities of each of the single-die states.

For fair dice we assume that each single-die state is equally probable, so each of the 24 two-die microstates is equally probable. Thus, the probability of each macrostate is simply the number Ω of microstates corresponding to that macrostate divided by the total number of microstates. That is, we just normalize the probability distribution by dividing the frequency of occurrence of each macrostate by the total number of microstates. This assures that $\sum_x P(x) = 1$.

Example

For example, the probability of occurrence of the macrostate of the dice having the sum of 8 is $\Omega(8)/24 = 3/24 = 1/8$.

Sum:	2	3	4	5	6	7	8	9	10
Ω:	1	2	3	4	4	4	3	2	1

Homework

HW Problem

Throw three fair 6-sided dice. What is the probability that at least one will show 6? Do this calculation in two ways:

a. Make use of the probability that a given die will show 6.

b. Make use of the probability that all three dice will *not* show 6.

Your answers should agree.

Homework

HW Problem

a. Find the probability of n heads in a simultaneous toss of N coins.

b. Which value of n is most probable.

c. Now consider the probability $P(x)$ of the fraction of heads $x = n/N$. Let $P_{\max}$ denote the probability of the most probable value of n for any given N. For $N = 6$, 40, and 200 plot (all on the same graph) the ratio $P(x)/P_{\max}$, for x ranging from 0 to 1. What can you conclude from comparison of the three plots?

Exercise—Dinner at Hogwarts Academy

A dinner is to be held at Hogwarts, and the following 13 students are to sit at the same table, a round table at which 15 chairs are placed:

Harry (Potter)	Hermione (Granger)	Ron (Weasley)
Ginny (Weasley)	Draco (Malfoy)	Vincent (Crabbe)
Gregory (Goyle)	Theodore (Nott)	Orla (Quirke)
Luna (Lovegood)	Michael (Corner)	Ernie (Macmillan)
Oliver (Wood)		

Two seats will remain empty. What is the probability that the students will sit in an arrangement such that their (first) initials spell out the word “Voldemort” clockwise as seen from above? Treat all arrangements that are identical apart from a rotation as equivalent.

Our second toy system—the two-state paramagnet

The constituents are spin-1/2 particles that interact at most weakly with each other. Each spin has two possible orientations with respect to an external magnetic field (recall the Stern-Gerlach experiment). These two orientations differ in energy, $E = -\boldsymbol{\mu} \cdot \mathbf{B}$, and at finite temperature some of the spins are in the higher-energy state.

The single-particle states are the two orientations of the magnetic moment. The microstates of the system are characterized by enumeration of the sequence of states of the individual moments. And the macrostates are characterized by the average number of moments in the up direction.

The number of microstates corresponding to each macrostate is

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} .$$