Reading assignment

Schroeder, section 2.3.

Recap of lecture 5

- Odds are everything in statistical mechanics.
- Number of distinct sequences of n integers from $1, \ldots, N$: N^n (N possibilities for each.)

$$\boxed{?}\boxed{?}\boxed{?} \ldots \boxed{?} \qquad\qquad 1\ 2\ 3\ \ldots\ N$$
$$1 \quad 2 \quad 3 \quad \ldots \quad n \qquad\qquad 1\ 2\ 3\ \ldots\ N$$
$$1\ 2\ 3\ \ldots\ N$$
$$\vdots$$

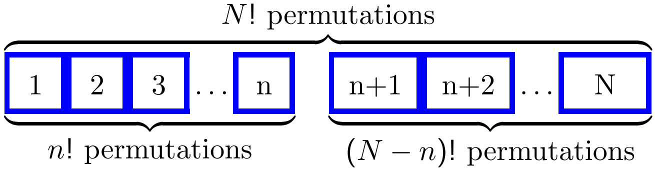
- Number of distinct sequences with no repetition within: $N(N-1)\cdots(N-n+1) = \frac{N!}{(N-n)!}$. Implies $N!$ permutations of N objects.

$$\boxed{?}\boxed{?}\boxed{?} \ldots \boxed{?} \qquad\qquad 1\ 2\ 3\ \ldots\ N$$
$$1 \quad 2 \quad 3 \quad \ldots \quad n$$

Recap of lecture 5

- Number of ways to choose n objects from a pool of N:

$$\frac{N!}{n!(N-n)!} = \binom{N}{n} \quad \text{(binomial coefficient)}\,.$$



Constituent states, 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" (constituent) 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 ordered 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 belonging to 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

$$\sum_x P(x) = 1 \, ,$$

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 (constituent) 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 belonging 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?

Homework

HW Problem

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.

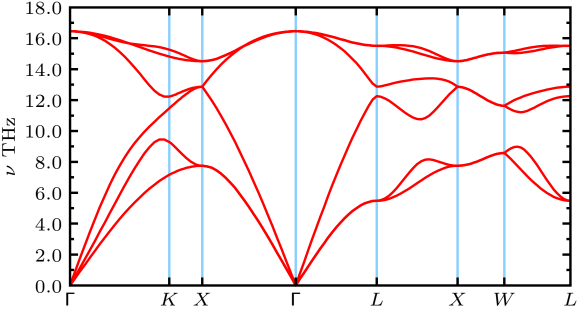
The single-particle states are the two orientations of the magnetic moment. The microstates of the system are characterized by enumeration of the sequence of states of the individual moments. And the macrostates are characterized by the average number of moments in the up direction.

The number of microstates corresponding to each macrostate is

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

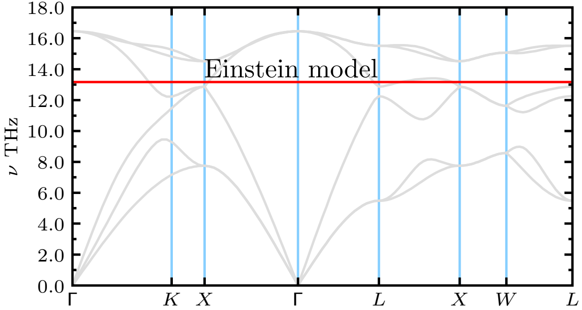
Our third toy system: the Einstein model

Recall that the vibrations of a crystal lattice can be described in terms of (Fourier) superposition of harmonic waves, each of which corresponds to a quantum harmonic oscillator. In reality, the frequency *vs* wavevector relations for the normal modes of vibration of a crystal are quite complicated:



Our third toy system: the Einstein model

But Einstein's idea was to treat the simplest possible quantized system, a collection of harmonic oscillators, all having the same frequency. This captures the effect of quantization on the thermodynamics without the distraction of real dispersion relations:



The states of the Einstein crystal

Since the constituents are all identical oscillators, the constituent (single-particle) states are those of a quantized harmonic oscillator:

$$\left(n + \frac{1}{2}\right)\hbar\omega\,,$$

and they are characterized by the quantum number n, which represents the number of quanta of excitation of the oscillator. The microstates of the entire system are then characterized by the entire set of quantum numbers of the constituents $\{n_i\}$. For example, if the system has 4 oscillators, one of its microstates has

$$n_1 = 2 \quad n_2 = 0 \quad n_3 = 1 \quad n_4 = 3\,.$$

The states of the Einstein crystal

The total energy of a particular microstate, let's call it j, is just the sum of the energies of the constituents:

$$E_j = \sum_{i=1}^{N} \left(n_i^{(j)} + \frac{1}{2} \right) \hbar\omega = \frac{N}{2}\hbar\omega + \left(\sum_{i=1}^{N} n_i^{(j)} \right) \hbar\omega \,.$$

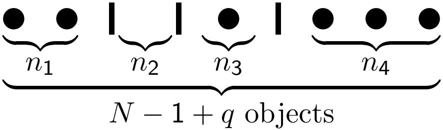
The macrostates will be characterized by the total energy. That is, all microstates having the same total energy belong to the same macrostate. Clearly, the only number needed to characterize that value is the sum of the quantum numbers of the constituents:

$$q = \left(\sum_{i=1}^{N} n_i^{(j)} \right) \,,$$

the total number of quanta of excitation in the system.

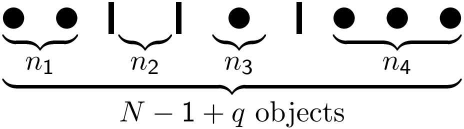
The states of the Einstein crystal

To determine the probability of macrostate q, we need to find the number Ω of microstates of the N constituents having a total of q quanta. That is, we need to find the number of ways we can partition the number q into N pieces.
An easy way to do this is to think of q dots in a row, with $N-1$ dividers separating the dots into N groups:



The number of ways of arranging the dots and dividers giving unique sequences of the n_i gives the number of microstates (note that the order of the n_i does matter here—the oscillators are considered distinguishable).

The states of the Einstein crystal



The result is the number of permutations of the $N-1+q$ dots and dividers divided by the number of permutations of the q dots (they are indistinguishable) and the number of permutations of the $N-1$ dividers alone (they are also indistinguishable.)

Number of microstates in macrostate $q =$

$$\frac{(N-1+q)!}{q!\,(N-1)!} = \binom{N-1+q}{q}.$$