Statistical Mechanics at Equilibrium, Part 1

Last time

Magnetic Properties of Materials

Today

Microstates

Configurations

Most probable configuration

Next time

Temperature

Partition functions

Questions please!

I encourage you to ask questions—that's the main advantage of being able to attend lectures in person



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Overview so far, and where to next

So far, we mostly looked at solids

Crystals only exist at low temperature

They are the lowest-energy arrangement of the atoms



For the rest of this unit, we will dial up the temperature

First, we will develop the tools to explain systems that are *not* in their ground state: statistical mechanics and thermodynamics



Statistical mechanics

Statistical mechanics explains how the microscopic properties of individual particles give rise to the macroscopic properties.

Along the way, we will answer important questions that affect all of chemistry, including:

- What is equilibrium?
- What drives a system to equilibrium?
- What is entropy?
- What is special about temperature?

Statistical mechanics

What can we know about a large collection of (say, $\sim 10^{23}$) molecules?

A large system cannot (normally) be completely specified. Instead, our knowledge is limited to the values of bulk parameters such as the number of molecules, temperature, pressure, volume…

Some quantities have no counterpart in individual molecules and are purely properties of a system.

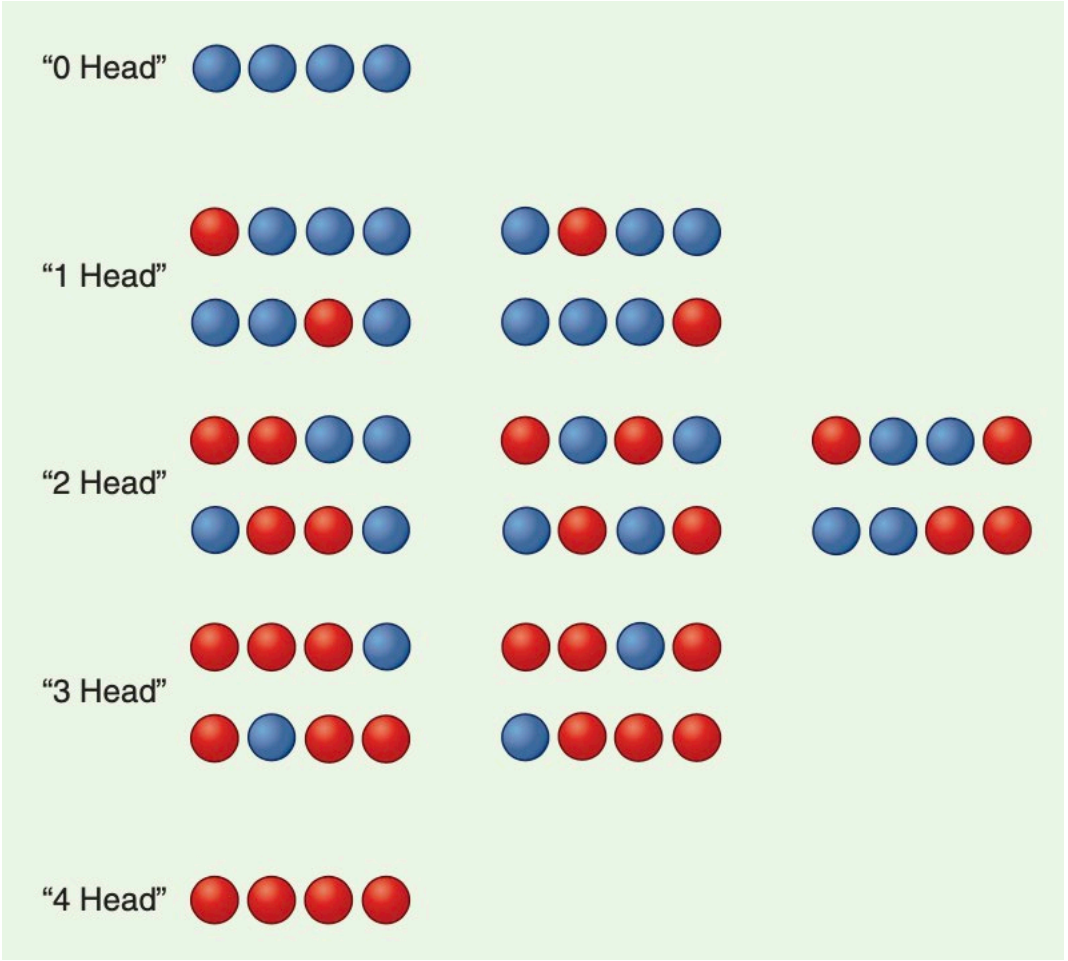
In statistical mechanics, even incomplete knowledge can tell us a lot about systems of molecules. But we first need to understand statistics and probability in chemical systems.

Microstates and configurations

What happens if we flip four coins?

Microstates: which coins are heads or tails (microscopic properties)

Configurations (macrostates): how many heads are there (macroscopic property)



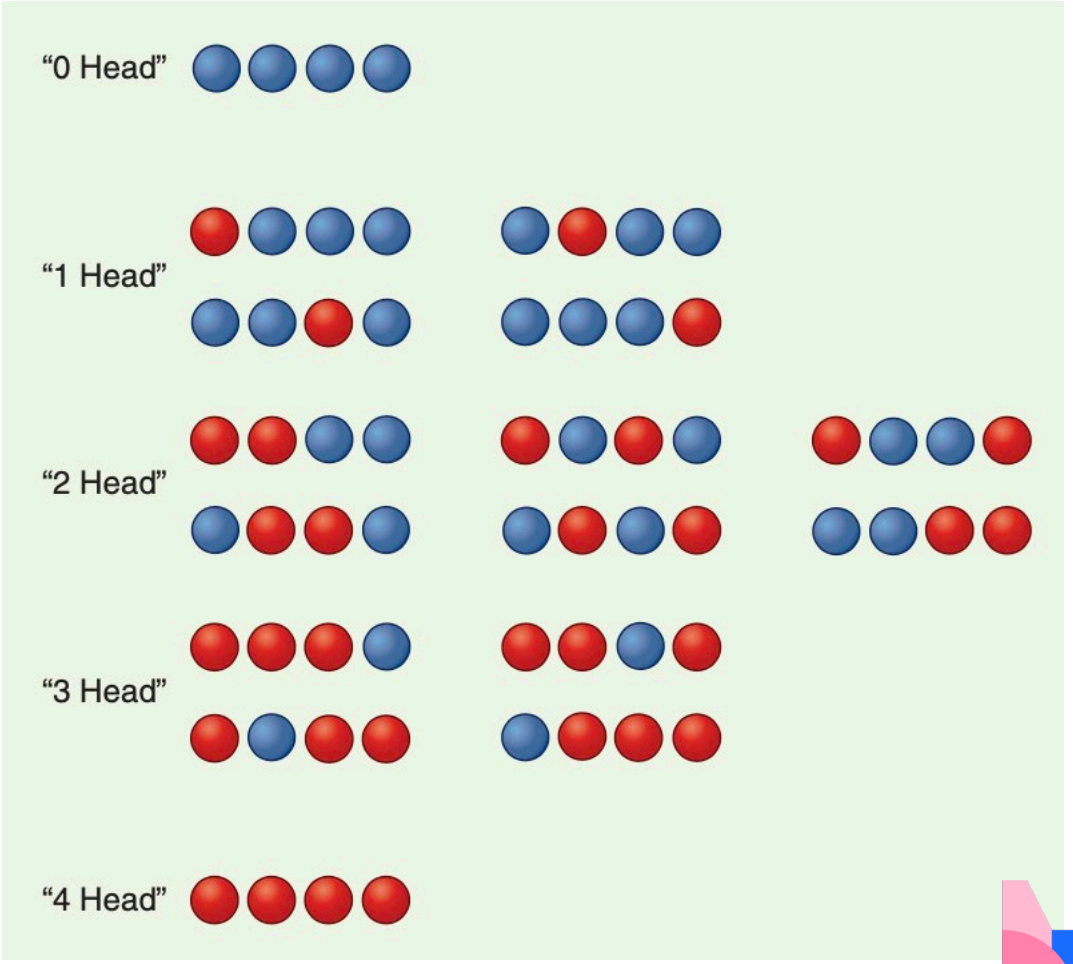
Microstates and configurations

Fundamental postulate:

All microstates are equally probable

Therefore, the most likely configuration is the one with the most microstates

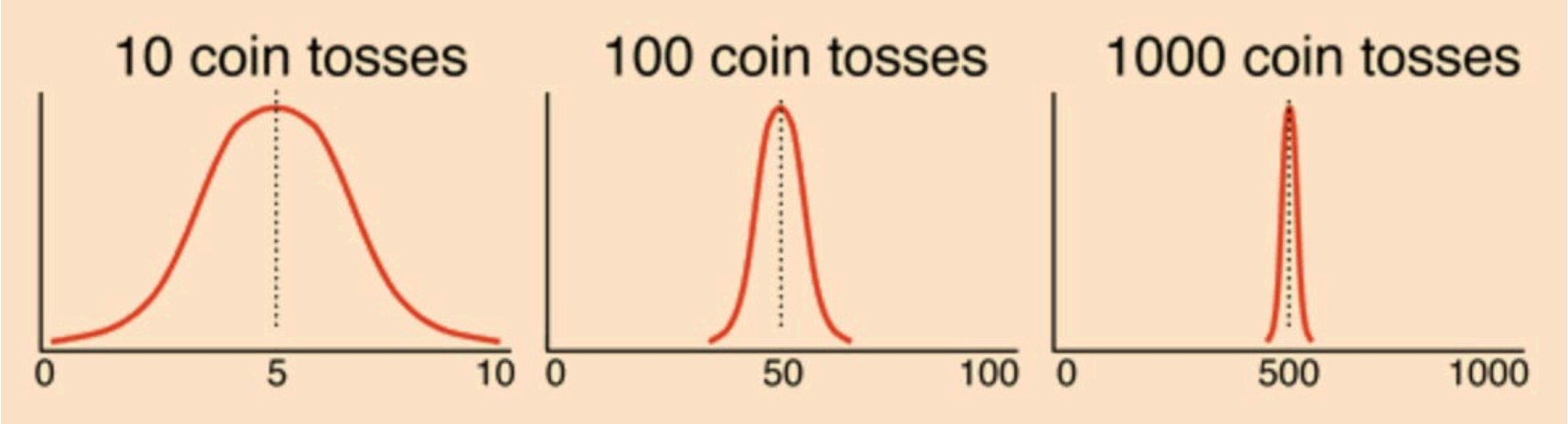
In this example, 2 heads



Mentimeter

Dominant configuration

As more coins are tossed, the distribution becomes more sharply peaked and the most likely configuration becomes *dominant*.



Chance of 4 heads: 0.205

Chance of 40 heads: 0.0108

Chance of 400 heads: $4.6 \cdot 10^{-11}$

In the thermodynamic limit ($N \rightarrow \infty$), only the dominant configuration is seen.

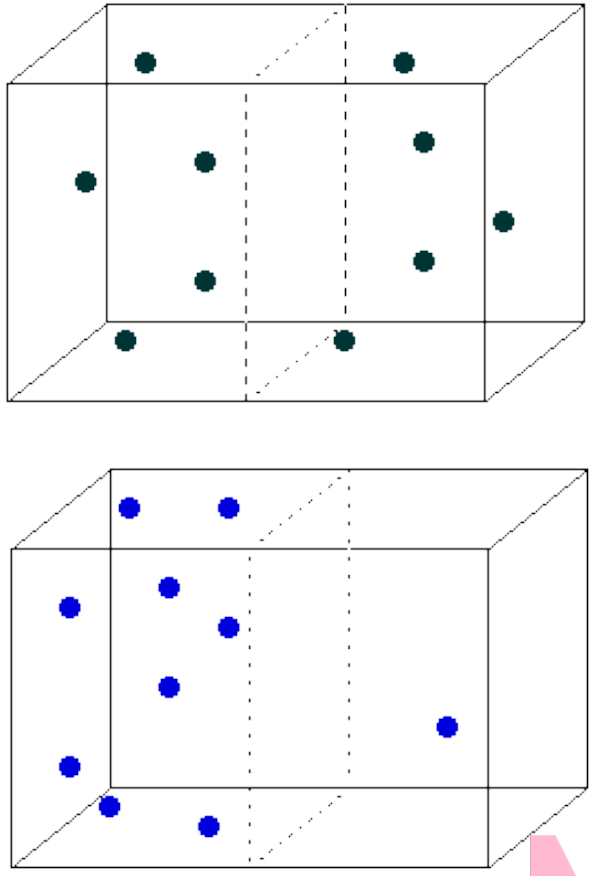
Dominant configuration

Another example: Molecules of air in a room have a 50:50 chance of being in left or right half.

In a 40 m^3 room, there are 10^{27} molecules.

The probability that more than 51% of the air is on the left is, very roughly, $e^{-10^{23}}$

99% of the time, the number of molecules in each half varies by less than 1 part in 10^{16}

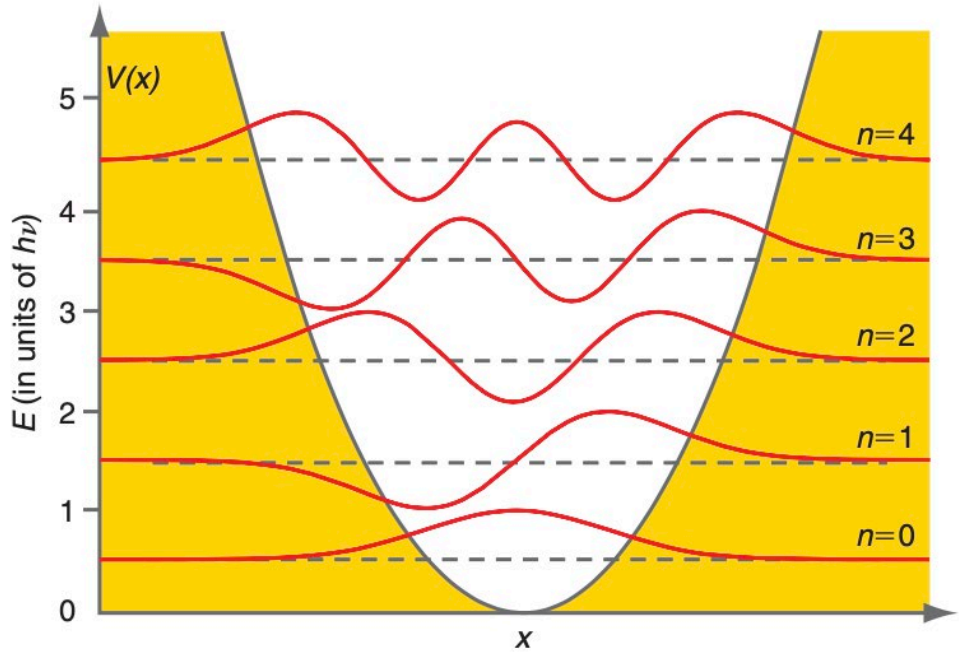


Mentimeter

Molecular configurations

In chemistry, the (discrete) quantum states are what's counted

Example: harmonic oscillator



$$E_n = h\nu\left(n + \frac{1}{2}\right)$$

Ignoring the constant zero-point energy:

$$E_n = h\nu n$$

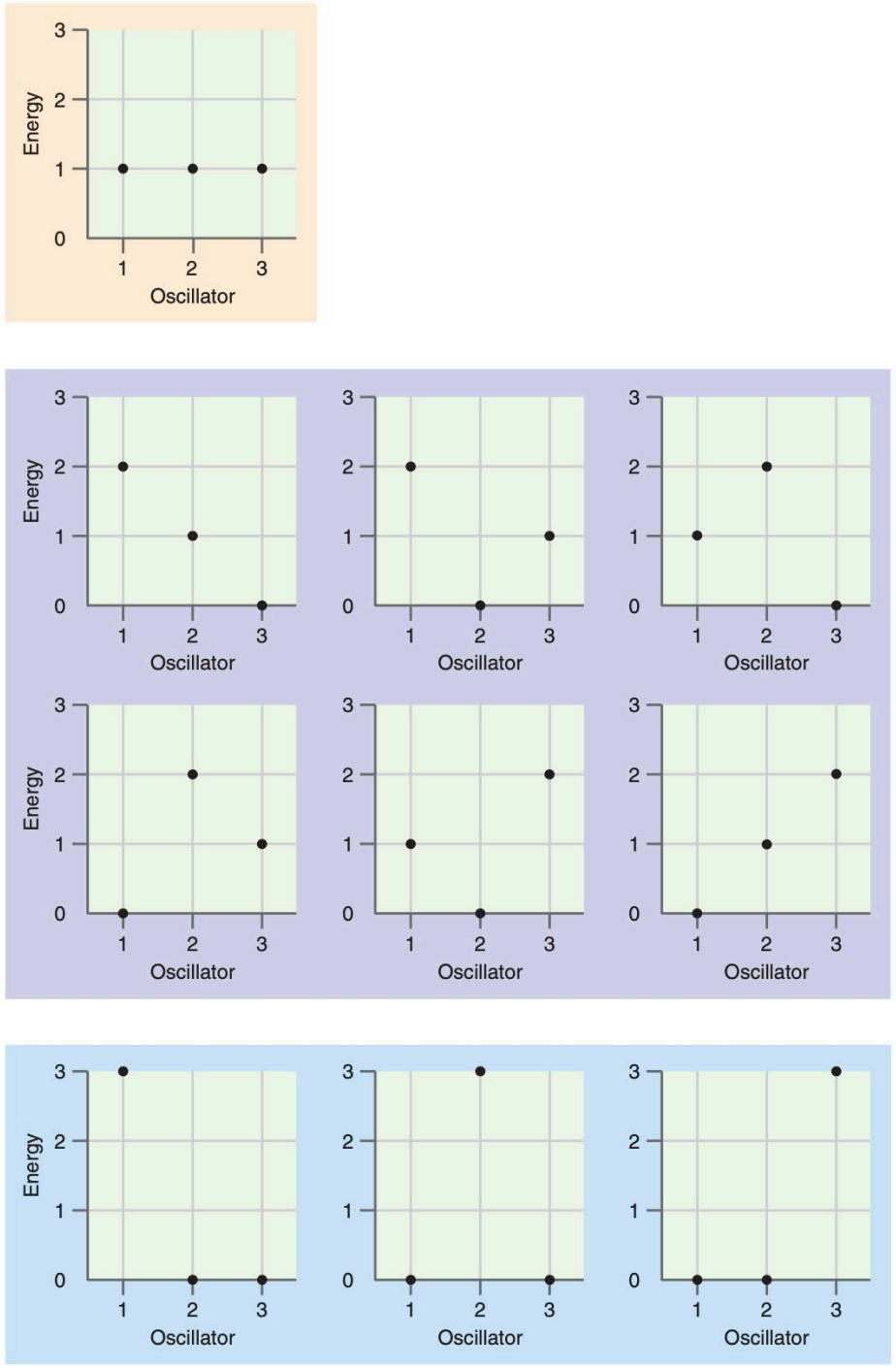
Molecular configurations

In chemistry, the (discrete) quantum states are what's counted

At right: 3 quanta of energy distributed over 3 distinguishable oscillators

We can label the configurations by the *populations* or *occupation numbers* of the quantum states, i.e. how many molecules are in a particular state?

Occupation number: n_i molecules in state i



Molecular configurations

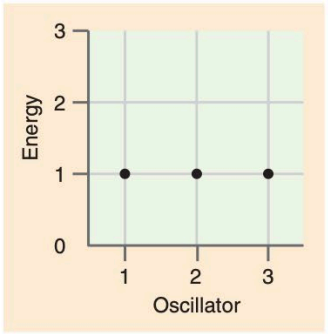
Orange configuration:

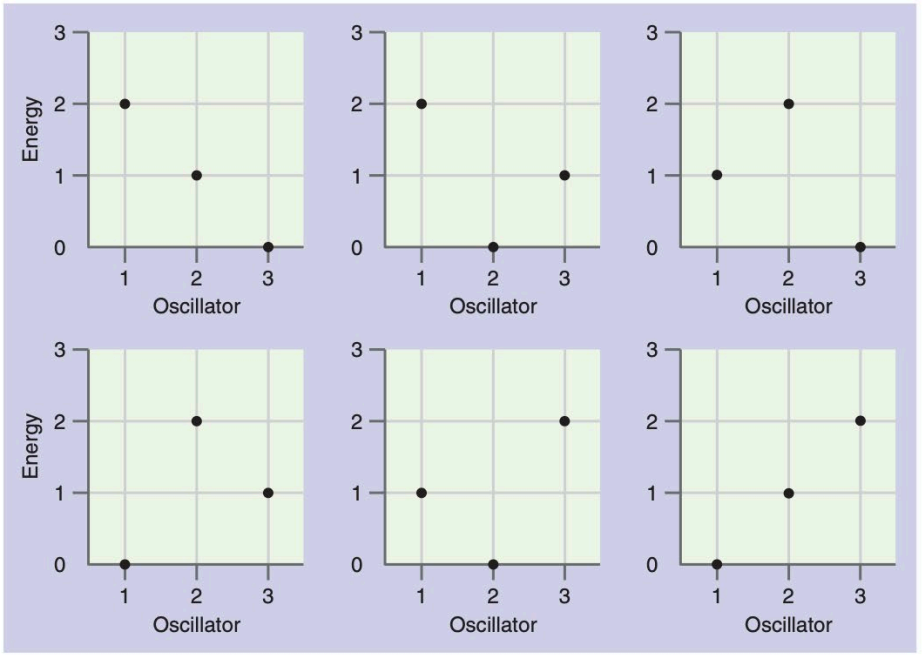
$$n_0 = 0$$
$$n_1 = 3$$
$$n_2 = 0$$
$$n_3 = 0$$

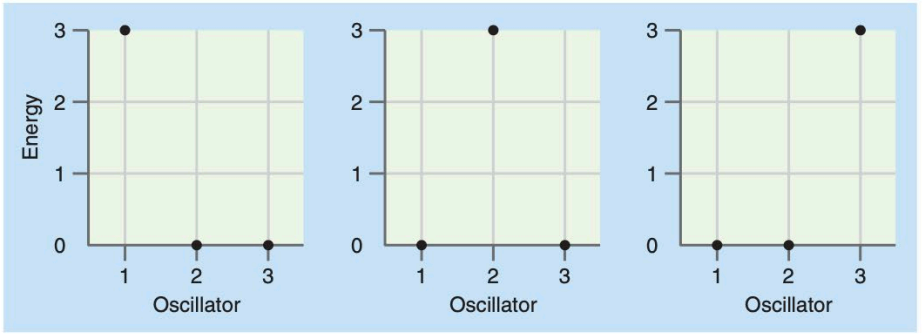
Or {0, 3, 0 0} for short

Purple configuration {1, 1, 1, 0}:

Looks more likely with probability 6/10







How many microstates?

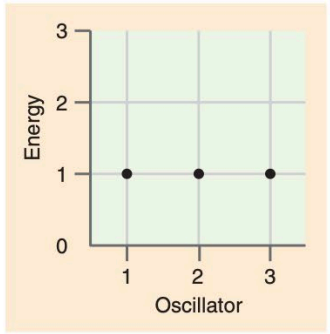
The weight of a configuration (number of corresponding microstates) is

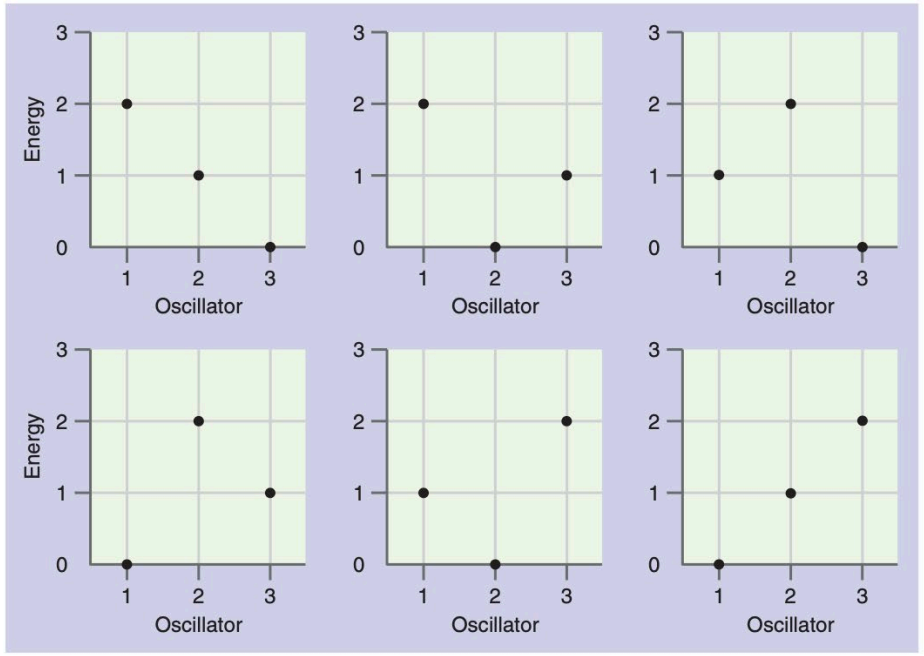
$$W\left(n_0, n_1, n_2, \ldots\right) = \frac{N!}{n_0! n_1! n_2! \cdots}$$

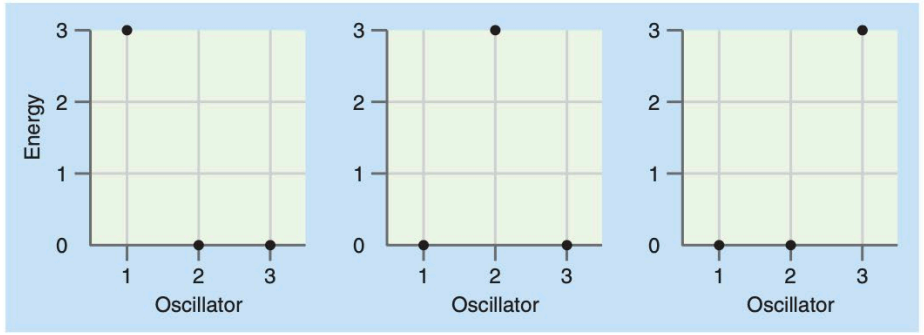
using the factorial $n! = n(n-1)(n-2)\cdots 2 \cdot 1$

E.g., blue configuration

$$W(2,0,0,1) = \frac{3!}{2!0!0!1!} = \frac{6}{2 \cdot 1 \cdot 1 \cdot 1} = 3$$

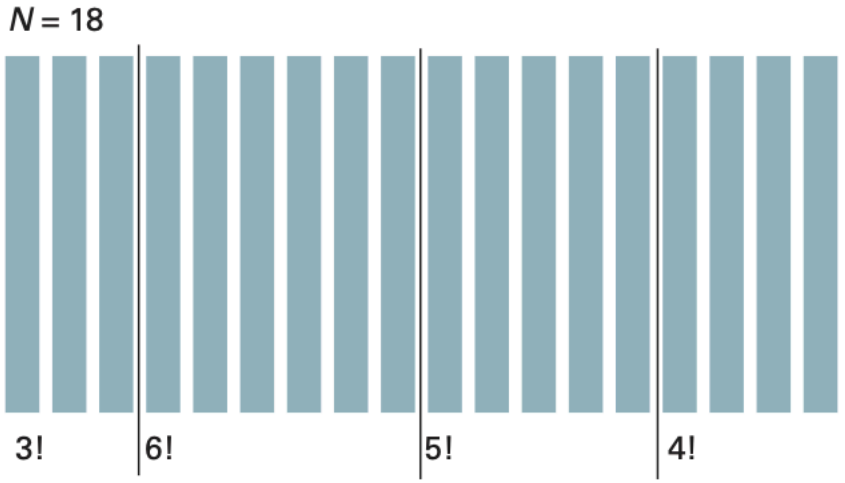






How many microstates?

Why $W\left(n_0, n_1, n_2, \ldots\right) = \dfrac{N!}{n_0! n_1! n_2! \cdots}$



Consider distributing *N* balls into bins.

N! ways of ordering the balls for distribution.

In bin *i*, there would have been $n_i!$ ways to choose the same n_i balls, which would be the same microstate.

Therefore, the total *N*! has to be divided by each of the $n_i!$ to avoid double counting

$$W = \frac{18!}{3!6!5!4!}$$

Mentimeter

Equilibrium is the dominant configuration

For given *N* and *E* (i.e., in an isolated system), equilibrium *is* the one dominant configuration.

If a system started out in a non-equilibrium microstate, the jostling and exchange of energy between molecules would eventually lead it towards the equilibrium configuration.

Once in equilibrium, it is astronomically unlikely that the system will fluctuate substantially from equilibrium.

The system will continue to change its microstate, but these will all be overwhelmingly likely to correspond extremely closely to the same configuration.

Finding the dominant configuration

We want to find the configuration with the largest weight

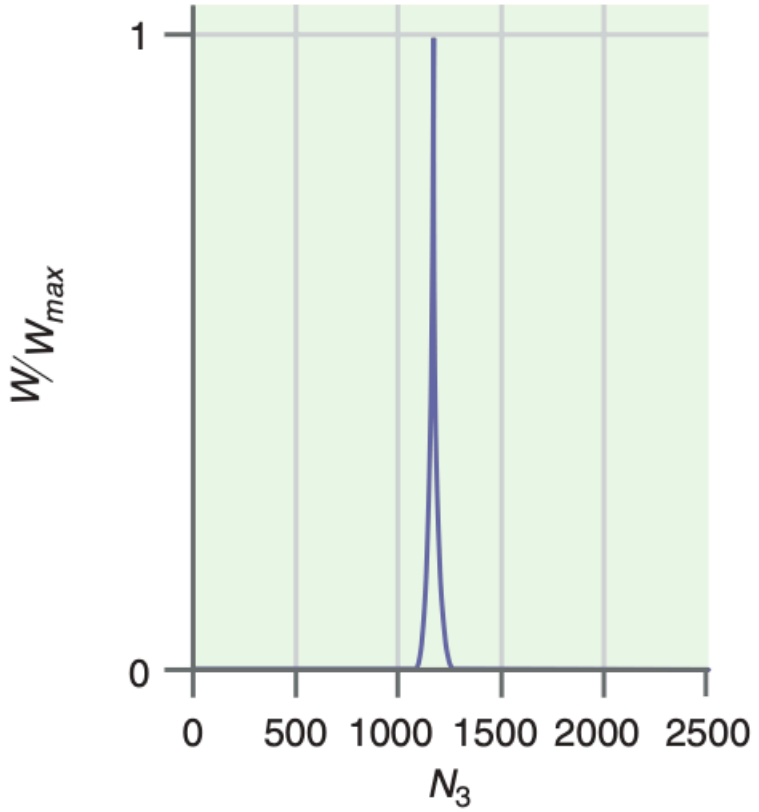
$$W\left(n_0, n_1, n_2, \ldots\right) = \frac{N!}{n_0! n_1! n_2! \cdots}$$

as a function of all n_i

Stirling's approximation: $\ln n! \approx n \ln n - n$

So we want to maximise

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$



Finding the dominant configuration

So we want to maximise

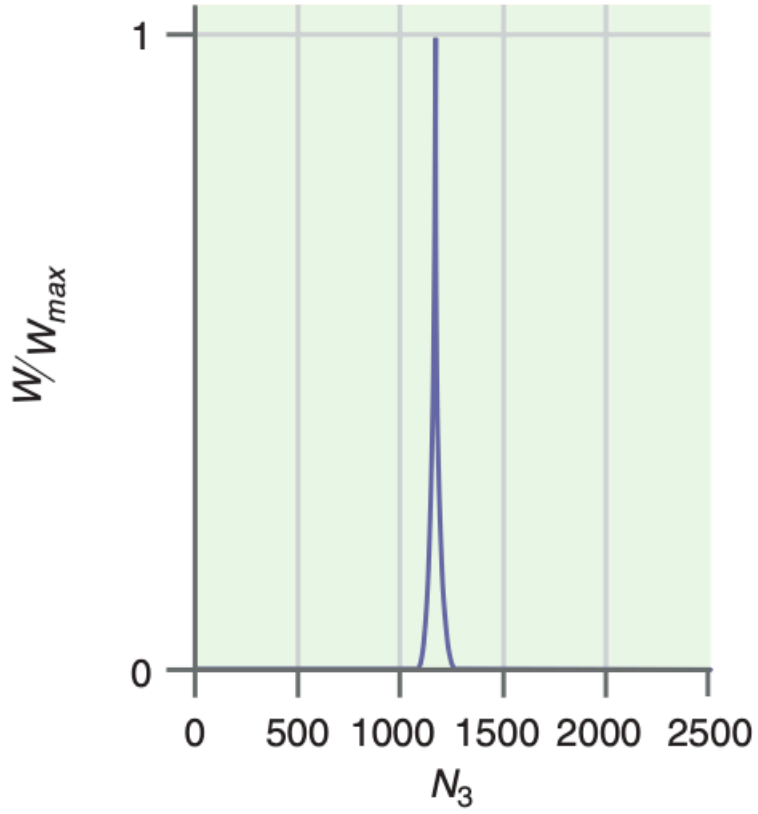
$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

as a function of all n_i

We are subject to two constraints:

1. Fixed number of molecules: $\sum_i n_i = N$

2. Fixed total energy: $\sum_i \varepsilon_i n_i = E$



The dominant configuration

The optimisation problem can be solved using Lagrange multipliers (see text).

Result: At equilibrium, the probability p_i of occupying energy level *i* is given by the *Boltzmann distribution:*

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

The denominator is central to statistical thermodynamics and is called the *partition function*:

$$q = \sum_i e^{-\beta\varepsilon_i}$$

Boltzmann distribution

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

Some remarks:

1. The single parameter β determines the most probable populations of all the states of the system
2. As the energy of a state rises, its occupation drops exponentially
3. The ratio of populations of two states is $\frac{n_i}{n_j} = \frac{e^{-\beta\varepsilon_i}}{e^{-\beta\varepsilon_j}} = e^{-\beta(\varepsilon_i - \varepsilon_j)}$

Mentimeter

Boltzmann distribution

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

So what is β?

We will see next time that $1/\beta$ behaves like the temperature.

More precisely, we'll *define* temperature so that

$$\beta = \frac{1}{kT}$$

Summary

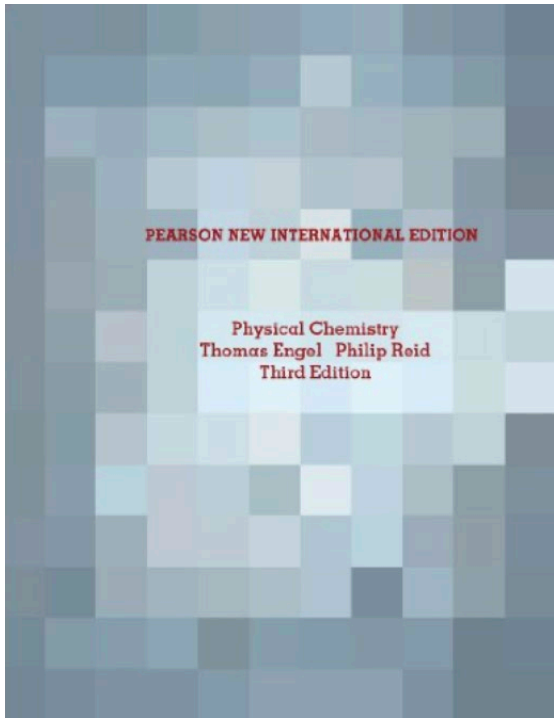
Key points:

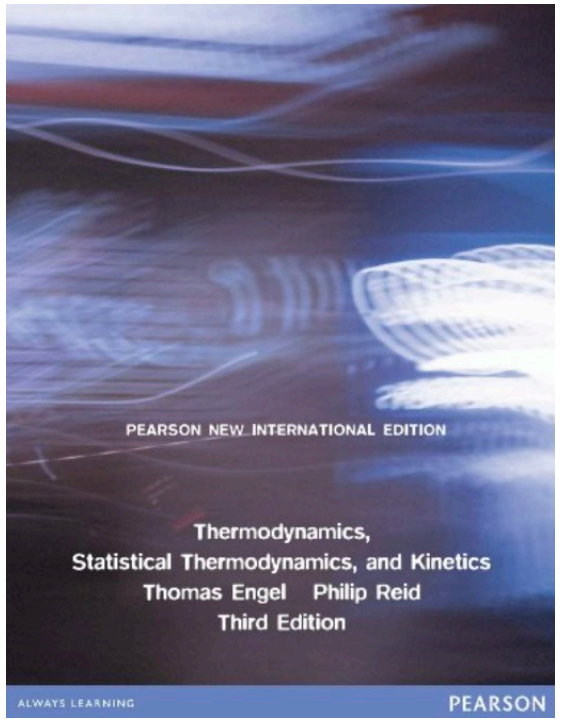
- Microstates: arrangements of individual molecules
  Configurations: collections of microstates giving the same bulk properties
- Some properties describe individual molecules and others only exist for entire chemical systems
- All microstates are assumed to be equally likely
  To find the probability of a configuration, count microstates
- In the thermodynamic limit, the most probable configuration dominates all others and defines the equilibrium of the system
- Occupations and probabilities at equilibrium follow the Boltzmann distribution

Reading

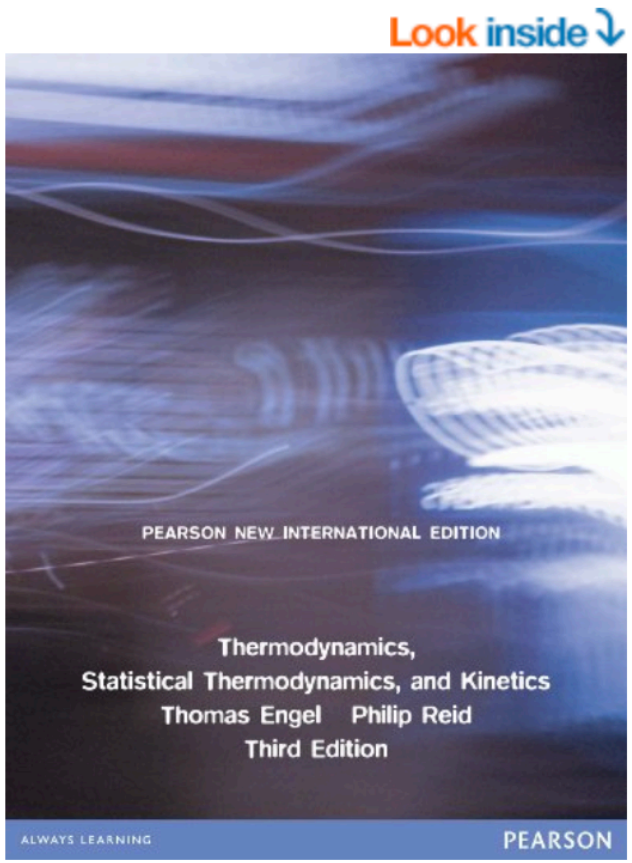
Engel and Reid, *Physical Chemistry*, 3rd ed. **OR**

Engel and Reid, *Thermodynamics, Statistical Thermodynamics, & Kinetics*, 3rd ed.





Reading



Thermodynamics, Statistical Thermodynamics, & Kinetics: Pearson New International Edition PDF eBook 3rd Edition, Kindle Edition

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Next time

Next time, we will show that $1/\beta$ behaves like the temperature

We'll discuss the physical meaning of the partition function

Reading:

Engel and Reid 30 (*Phys. Chem.*) / 13 (*Thermo.*)