Lecture 10a: Boltzmann distribution

Learning objectives: After this lecture, you will be able to:

1. Explain the origin of random molecular motion in fluids

2. Explain how the barometric pressure formula can be used to motivate the Boltzmann distribution

3. Interpret the meaning of the Boltzmann distribution and describe its range of applicability (i.e. systems in thermal equilibrium)

4. Describe how temperature affects the Boltzmann distribution of systems

Pre-reading: Most of this lecture will be new to you, but we will rely heavily on the barometric pressure formula that you used in Lecture 8b, Activity 1. Please review it, and our expression for density as a function of height.
Activity 1: Statistical interpretation of the barometric formula

Your friend is at a football game (that isn’t well attended), but she didn’t tell you where she’s sitting. Section 1 has, on average, 3 people in each row of 20 seats. Section 2 has, on average, 12 people in each row of 20 seats.

1. Assuming the sections have the same total number of seats and that your friend chose their seat at random, in which section are you more likely to find your friend? How much more likely are you to find your friend in that section, compared to the other section?

   Section 2
   4 times more likely

Your very special pet air molecule escaped into the atmosphere, but it didn’t tell you where it went. (It has been randomly bumped around by all the other air molecules so it could be anywhere!) It stands to reason that wherever there are more molecules, the better your chance is of finding your molecule there. How much more likely it is that you would find the molecule at height $y_2 = 0$, near the ground, versus at height $y_1 = 8$ km near the top of Mount Everest?

2. From the expression for pressure as a function of height in a gas (see page 1) and the ideal gas law (in the form $P = \frac{\rho}{m} T$) find an expression (no numbers yet) for the density as a function of height $\rho(y)$.

   Assume $T$ is constant.

   \[ \rho = \left( \frac{m}{k_B T} \right) \rho(y) = \frac{m}{k_B T} \rho_0 e^{-y/H} = \rho_0 e^{-y/H} \]

3. Find an expression for the number of molecules in a volume of air $V$, in the atmosphere, as a function of $y$: $N(y)$. Keep in mind that density can be written $\rho = \frac{\text{mass}}{V} = \frac{\text{mass of 1 molecule}}{V} \cdot N$; where $N$ is the number of molecules in volume $V$.

   \[ N(y) = \frac{V}{m} \rho(y) = \frac{V}{m} \rho_0 e^{-y/H} \]

4. By comparing the number of molecules in a volume of air $V$ at height $y_2$ to the number of molecules in that same size volume of air $V$ at height $y_1$, show that the following is how much more likely you are to find your molecule at $y_2$ compared to finding it at $y_1$:

   \[ \frac{\text{Prob}(y_2)}{\text{Prob}(y_1)} = \frac{N(y_2)}{N(y_1)} = \frac{\frac{V}{m} \rho_0 e^{-y_2/H}}{\frac{V}{m} \rho_0 e^{-y_1/H}} = e^{-\frac{(y_2 - y_1)}{H}} \]

   $H = \frac{k_B T}{m g}$

5) So, how much more likely are you to find your pet air molecule near the ground, versus near the top of Mount Everest?

   $y_2 = 0$, $y_1 = 8$ km

   \[ \text{Prob(ground)} = e^{-\frac{(0 - 8\text{ km})}{H}} \]

   $8\text{ km}$

   \[ \text{Prob(Everest)} = e^{-\frac{8\text{ km}}{H}} = e^{-\frac{8\text{ km}}{8\text{ km}} \text{ H}} = e^{-\frac{1}{2}} \approx 0.632 \]
Activity 2: Boltzmann distribution

The Boltzmann distribution says that given some particles or molecules in a fluid, and any kind of potential energy $U$, the probability of a given particle having energy $U_2$ relative to $U_1$ is:

\[
\frac{\text{probability of observing system in state } 2}{\text{probability of observing system in state } 1} = e^{\frac{\Delta U}{k_B T}}, \text{ where } \Delta U = U_2 - U_1
\]

Let's use this to understand our football stadium (as an analogy).

1. Is the gravitational potential energy of a person in section 1, $U_1$, or potential energy of a person in section 2, $U_2$ greater?

2. Using the Boltzmann distribution (as an analogy), argue that it is more probable to find your friend in section 2 compared to section 1. That is, think about whether the quantity \( \frac{\text{probability of friend in section 2}}{\text{probability of friend in section 1}} \) is greater or less than 1.

3. Using the Boltzmann distribution, show how much more probable it is to find your lost pet gas molecule near the ground, compared to at a height $y$ above the ground? Express the answer in terms of $T$, $k_B$, $g$, and $m$. Hint: $\Delta U = mg\Delta h$.

\[
\frac{\text{Prob}(y_2)}{\text{Prob}(y_1)} = e^{-\frac{[U(y_2) - U(y_1)]}{k_BT}} = e^{-\frac{mg(y_2 - y_1)}{k_BT}}
\]

Does this look like a result from the previous page?

3. Consider a very tall sealed container of gas. As the temperature of the gas is increased what happens to the probability of finding a randomly chosen gas molecule at the top of the container? The probability: (explain your answer choice)

(a) increases
(b) decreases
(c) does not change
(d) it depends on the kind of gas that is used

(hint: this is kind of like giving away free, caffeinated Pepsi in the stadium)
Practice Problems

Attempt to provide an explanation why the gas molecules don't simply fall to the ground. Why do they stay up in the atmosphere?

There are two possible conformations (states) of 1-methylcyclohexane:

1. At thermal equilibrium at 298K, 95% of the molecules are in the equatorial conformation. What is the difference in energy $\Delta U$ between these two conformations?
   
   (a) equatorial is more stable by about 19 $k_B T$
   (b) axial is more stable by about 19 $k_B T$
   (c) equatorial is more stable by about 3 $k_B T$
   (d) axial is more stable by 3 $k_B T$

2. Consider the same molecule as in problem 1. At approximately what temperature would 50% of the molecules be in conformation 2?

   (a) 0K
   (b) 330K
   (c) 433K
   (d) 600K
   (e) none of the above

$P_2/P_1 = 0.5/0.5 = 1$

$P_2/P_1 = e^{-(u_2-u_1)/k_B T}$

$T \to \infty \Rightarrow e^{-(u_2-u_1)/k_B T} \to 1$

Bonus: HAVE A WONDERFUL THANKSGIVING BREAK!!!