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.

Hydrostatic Pressure (Fluids)

\[ P_1 = P_0 + \rho_w gh \]

\[ \rho_{water} = 1000 \text{ kg/m}^3 \]

Barometric Pressure (Air)

\[ P_1 = P_0 e^{-\frac{y}{H}} \]

\[ H = \frac{k_B T}{\frac{m}{\bar{m}}} \approx 8 \text{ km} \]

\[ \bar{m} = 29 \text{ amu on Earth} \]
Activity 1: Statistical interpretation of the barometric formula

Your very special pet air molecule escaped into the atmosphere and you want to know where it is likely to be. It has been randomly bumped around by all the other air molecules so it could be anywhere! But it stands to reason that wherever there are more molecules, the better your chance is of finding your molecule there. So, we will figure out how much more likely it is that you would find the molecule at height $y_1$ at the roof of your house, versus at height $y_2$ at the top of the mountain next to your house...

1. From the expression for pressure as a function of height in a gas (see page 1) and the ideal gas law (in the form $P = \frac{P_0}{m} k_B T$) find an expression for the density as a function of height $\rho(y_1)$. Assume $T$ is constant.

   \[ \rho(y) = \frac{P_0}{k_B T} = \frac{m}{k_B T} P e^{-\frac{mg y}{k_B T}} = \rho_0 e^{-\frac{mg y}{k_B T}} \]

2. Calculate the ratio of the densities of the gas at these two heights $\frac{\rho(y_2)}{\rho(y_1)}$ in terms of $m$, $g$, $k_B$, $T$, $y_1$, and $y_2$.

   \[ \frac{\rho_0 e^{-\frac{mg y_2}{k_B T}}}{\rho_0 e^{-\frac{mg y_1}{k_B T}}} = e^{-\frac{mg (y_2 - y_1)}{k_B T}} \]

3. Someone says: “Hey, if I choose a molecule at random (like your pet molecule), the probability it is at height $h$ is proportional to the density of the atmosphere at height $h$”. Do you agree with this statement?

   Yes, more particles means better chance of one of those being the randomly chosen one.

4. Make an argument that we get the ratio of the probabilities to be:

   \[ \frac{\text{probability}(y_2)}{\text{probability}(y_1)} = e^{-\frac{mg (y_2 - y_1)}{k_B T}} \]

   \[ \begin{align*}
   \rho_2 &= \frac{N_2 m}{V} \\
   \rho_1 &= \frac{N_1 m}{V} \\
   \frac{\rho_2}{\rho_1} &= \frac{N_2}{N_1} \frac{m/v}{m/V} = \frac{N_2 m/v}{N_1 m/V} = \frac{N_2}{N_1} = e^{-\frac{mg (y_2 - y_1)}{k_B T}}
   \end{align*} \]

5. Consider a very tall sealed container of gas. As the temperature of the gas is increased, what happens to the concentration (or density) of gas molecules at the top of the container? (refer to result from question 1)

   The concentration: (explain your choice of answer)

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

   \[ \rho(y_2) = \rho_0 e^{-\frac{mg y_2}{k_B T}} \]

   \[ T \to 0, \quad \frac{mg y}{k_B T} \to 0, \quad \rho(y) \to 0 \]

   \[ T \to \infty, \quad \frac{mg y}{k_B T} \to 0, \quad \rho(y) \to \rho_0 \]

   \[ e^{-\frac{y}{k_B T}} = e^{-\frac{1}{k_B T}} \]
Activity 2: Boltzmann distribution

The probability distribution from the barometric formula $P(y_2) = e^{-mg(y_2 - y_1)/k_B T}$ is an example of a much more general relation called the Boltzmann distribution.

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

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 $U_1$.

"I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered."  --- Ludwig Boltzmann

Let's use the Boltzmann formula as a starting point to derive the barometric formula.

1. What is the probability to observe a randomly chosen gas molecule at height $y$ above the ground, in terms of $T$, $k_B$, $g$, $m$, and the probability of seeing the molecule right at the ground? Hint: Use the above equation with $\Delta U = mg\Delta h$, where State 2; molecule at height $y$, State 1; molecule at height $0$.

\[
\frac{\text{Prob}(y)}{\text{Prob}(y=0)} = e^{-\frac{U_{y+y} - U_{y+y=0}}{k_B T}} = e^{-\frac{-mg y}{k_B T}}
\]

\[
\text{Prob}(y) = \text{Prob}(y=0) e^{-\frac{-mg y}{k_B T}}
\]

2. What is the probability of observing a randomly chosen gas molecule at the top of the mountain at height $y_2$ compared to the probability of finding it at the height of your roof $y_1$. That is, calculate $\text{Prob}(y_2)$ in terms of $T$, $k_B$, $g$, $m$, and $\text{Prob}(y_1)$ using the Boltzmann distribution with appropriate $U_1$ and $U_2$.

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

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

Let's revisit the same problem, but this time, use the Boltzmann distribution to explain your choice of answer.

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 molecules at the top of the container? The probability: (explain your choice of answer)

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

   \[
   \frac{P_2}{P_1} = e^{-\frac{(U_2 - U_1)}{k_B T}}
   \]

   \[
   0.95 = e^{-\frac{(U_2 - U_1)}{k_B T}}
   \]

   \[
   0.05 = e\ln\left(\frac{0.95}{0.95}ight) = -\frac{(U_2 - U_1)}{k_B T}
   \Rightarrow 3 = \frac{(U_1 - U_2)}{k_B T}
   \]

   \[
   (U_1 - U_2) = 3k_B T
   \]

   \[
   U_1 > U_2
   \]

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

\[
\frac{P_2}{P_1} = e^{-\frac{(U_2 - U_1)}{k_B T}}
\]

\[
T \rightarrow \infty \quad e^{-\frac{(U_2 - U_1)}{k_B T}} \rightarrow 1
\]

Bonus: HAVE A WONDERFUL THANKSGIVING BREAK!!!
This page has been left blank
One-Minute Paper

Your name: ___________________________  TF: ___________________________

Names of your group members: ___________________________

- Please tell us any questions that came up for you today during lecture. Write “nothing” if no questions(s) came up for you in class.

- What single topic left you most confused after today’s class?

- Any other comments or reflections on today’s class?