Two central themes of this lecture

1. Apply probability arguments that describe coin flips and card picks to a physical system

2. Learn how distinguishable particles are statistically distributed in energy for systems with quantized energy levels

The various energy levels may be degenerate!
We will discuss the following three questions:

1. What is the probability of finding a particle with a given energy?
2. How many available energy states are in a system? - counting the states as a function of energy
3. The occupation number - how many particles in a particular energy state?

Eventually we will ask how indistinguishable particles are statistically distributed over the same quantized energies.
1. The Maxwell-Boltzmann Factor* - the probability of finding a particle with a given energy

Define the System:
- \( N=4 \) distinguishable particles (to illustrate the ideas)
- Equally spaced energies 0\( \epsilon \), 1\( \epsilon \), 2\( \epsilon \).... The allowed energies are now QUANTIZED.
- Add fixed amount of energy, say \( E_{\text{tot}}=5\epsilon \) (to illustrate the ideas)

Let \( n_1 \)=number of particles with energy \( \epsilon_1 \), etc.

How many available states does the system have for a fixed total energy of 5\( \epsilon \)?

Two constraints

\[
E_{\text{tot}}(n_1, n_2, \ldots, n_r=6) = \sum_r n_r \epsilon_r = 5\epsilon
\]

\[
N = \sum_r n_r = 4
\]

*Previously mentioned in Lecture 6.05
ALL Possible States for a Fixed Energy of $E_{\text{tot}} = 5\varepsilon$

State A:  

State B:  

State C:  

State D:  

State E:  

State F:  

Microscopic Model
How many microstates for each macrostate (let $E_{\text{tot}} = 5\epsilon$)?

Particles are distinguishable:

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

Equally Spaced Energy Levels; 4 Distinguishable Particles; Total Energy FIXED at $E_{\text{tot}} = 5\epsilon$

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>0\epsilon</th>
<th>1\epsilon</th>
<th>2\epsilon</th>
<th>3\epsilon</th>
<th>4\epsilon</th>
<th>5\epsilon</th>
<th>TOTAL E</th>
<th>Microstates W or $g(E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3 0</td>
<td>0 0 0 0</td>
<td>1</td>
<td>5\epsilon</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2 1</td>
<td>0 0 1 0</td>
<td>0</td>
<td>5\epsilon</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2 0</td>
<td>1 1 1 0</td>
<td>0</td>
<td>5\epsilon</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1 2</td>
<td>0 1 0 0</td>
<td>0</td>
<td>5\epsilon</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1 1</td>
<td>2 0 0 0</td>
<td>0</td>
<td>5\epsilon</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0 3</td>
<td>1 0 0 0</td>
<td>0</td>
<td>5\epsilon</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TOTAL 56
Probability that a particle will have a certain energy?

Equally Spaced Energy Levels; 4 Distinguishable Particles; Total Energy FIXED

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>0ε</th>
<th>1ε</th>
<th>2ε</th>
<th>3ε</th>
<th>4ε</th>
<th>5ε</th>
<th>TOTAL E</th>
<th>Microstates W or g(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>5ε</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1</td>
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<td>0</td>
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<td>0</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5ε</td>
<td>4</td>
</tr>
</tbody>
</table>

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Prob. that a particle has 0ε \(\equiv P(\varepsilon = 0)\)

\[
= \sum_{A}^{F} \left( \frac{\text{fraction of particles having } 0\varepsilon \times \text{probability that state will occur}}{\text{OR means add}} \right)
\]

\[
= \frac{3}{4} + \frac{4}{56} + \frac{2}{4} + \frac{12}{56} + \frac{2}{4} + \frac{12}{56} + \frac{1}{4} + \frac{12}{56} + \frac{0}{4} + \frac{4}{56} = \frac{21}{56}
\]

Prob. that a particle has 1ε \(\equiv P(\varepsilon = 1)\)

\[
= \frac{0}{4} + \frac{4}{56} + \frac{1}{4} + \frac{12}{56} + \frac{0}{4} + \frac{12}{56} + \frac{2}{4} + \frac{12}{56} + \frac{3}{4} + \frac{4}{56} = \frac{15}{56}
\]
Probability of finding a particle in a given energy state

<table>
<thead>
<tr>
<th>Situation</th>
<th>Symbol</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle w. 0ε</td>
<td>P(0ε)</td>
<td>21/56 = 0.375</td>
</tr>
<tr>
<td>particle w. 1ε</td>
<td>P(1ε)</td>
<td>15/56 = 0.268</td>
</tr>
<tr>
<td>particle w. 2ε</td>
<td>P(2ε)</td>
<td>10/56 = 0.178</td>
</tr>
<tr>
<td>particle w. 3ε</td>
<td>P(3ε)</td>
<td>6/56 = 0.107</td>
</tr>
<tr>
<td>particle w. 4ε</td>
<td>P(4ε)</td>
<td>3/56 = 0.054</td>
</tr>
<tr>
<td>particle w. 5ε</td>
<td>P(5ε)</td>
<td>1/56 = 0.018</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>56/56 = 1.00</strong></td>
</tr>
</tbody>
</table>

Average energy of a particle?

\[
\langle E \rangle = \frac{21}{56} \cdot 0\varepsilon + \frac{15}{56} \cdot 1\varepsilon + \frac{10}{56} \cdot 2\varepsilon + \frac{6}{56} \cdot 3\varepsilon + \frac{3}{56} \cdot 4\varepsilon + \frac{1}{56} \cdot 5\varepsilon = 1.25\varepsilon
\]
Probability Distribution

Fit to exponential

$E_{\text{total}} = 5\varepsilon$

allowed energies are now QUANTIZED

$e^{-\beta E}$
Why an exponential is a good guess?

\[ P(E)dE = \frac{n(E)}{N} dE = \frac{2}{\sqrt{\pi}} \frac{E^{1/2}}{(k_B T)^{3/2}} e^{-E/k_B T} dE \]

Equation from Appendix of L9.02 for ideal gas atoms

See Appendix of this lecture for a more fundamental discussion regarding the origin of the exponential
Generalizing - How are classical particles in a quantized system distributed in energy as number of particles becomes large?

Non-degenerate levels:

\[ P(E_a) \propto e^{-\left(\frac{E_a}{k_B T}\right)} \]
\[ P(E_b) \propto e^{-\left(\frac{E_b}{k_B T}\right)} \]

For case of degenerate levels:

You must identify the zero of energy!

\[ P(E_a) \propto g_a e^{-\left(\frac{E_a}{k_B T}\right)} \]
\[ P(E_b) \propto g_b e^{-\left(\frac{E_b}{k_B T}\right)} \]
from the Boltzmann Factor to the Boltzmann Equation

\[
\frac{P(E_b)}{P(E_a)} = \frac{g_b e^{-\left(\frac{E_b}{k_B T}\right)}}{g_a e^{-\left(\frac{E_a}{k_B T}\right)}} = \frac{g_b}{g_a} e^{-\left(\frac{(E_b-E_a)}{k_B T}\right)}
\]

But......

\[
P(E_a) = \frac{N_a}{N_{tot}} \quad P(E_b) = \frac{N_b}{N_{tot}}
\]

\[
\frac{P(E_b)}{P(E_a)} = \frac{N_b}{N_a} = \frac{g_b}{g_a} e^{-\left(\frac{(E_b-E_a)}{k_B T}\right)}
\]

\[E_b > E_a\]

The above equation is known as the **Boltzmann Distribution Equation** (different from Boltzmann probability distribution function). It determines the relative number of particles with a specified energy in a system with quantized energy levels. It assumes the system is in thermal equilibrium at some temperature T.
Example: The energy levels for a 2d infinitely high quantum well (see L5.01) are given below. If 15 particles are found in the energy level $8E_o$, how many will be in the energy level $13E_o$? Ignore spin.

Let $k_BT = 1.0 \ E_o$, $2.0 \ E_o$ and $5.0 \ E_o$.

If the particles have spin $\frac{1}{2}$, then $g_a = 2$, $g_b = 4$.
Up Next - The number of available states
APPENDIX: Where does the exponential in the Boltzmann factor come from? - a plausibility argument -

1. Maxwell-Boltzmann distribution for gas atoms contains an exponential function. Why?
2. The exponential naturally arises for N particles (N must be large enough to provide well-defined probabilities) when the sum of all energies is some constant $E_{\text{tot}}$.

A system with N particles. Total energy is fixed at $E_{\text{tot}}$. 
Experiment I: Pull two particles from the system and measure their energies:

- Probability that one particle has energy $E_1 = P(E_1)$
- Probability that the other particle has energy $E_2 = P(E_2)$
- Probability that particle one has energy $E_1$ AND particle two has energy $E_2$ is just $P(E_1) \cdot P(E_2)$

The probability that ALL other N-2 particles have an energy $E_{\text{tot}} - (E_1 + E_2)$ must equal the probability that one particle has energy $E_1$ AND the other particle has energy $E_2$.

This means that $P(E_1) \cdot P(E_2) = P(E_{\text{tot}} - E_1 - E_2)$  

EQ. I
Experiment II: Pull out one particle from the system and measure its energy:

- Probability that the one particle removed has energy $E_1 + E_2 = P(E_1 + E_2)$

- The probability that ALL other $N-1$ particles have an energy $E_{\text{tot}}-(E_1+E_2)$ must equal the probability that the one particle removed has energy $E_1 + E_2$

- This means that $P(E_1 + E_2)=P(E_{\text{tot}}-(E_1+E_2))$  \hspace{1cm} EQ. II

Comparing EQ. I and EQ. II, we must conclude that

$$P(E_1) \cdot P(E_2)=P(E_1+E_2)$$

What function might satisfy this simple relationship?
The only function $P(E)$ that behaves in this way is an exponential, so

$$P(E) \sim e^{(\text{const} \times E)} \sim e^{(- \beta E)}$$

The constant $-\beta$ is required to make the argument of the exponential have no units. It follows that

$$e^{-\beta E_1} e^{-\beta E_2} = e^{-\beta (E_1 + E_2)}$$

Other arguments not given here lead to the fact that $\beta = 1/k_B T$. See Appendix in Lecture 9.05.