Lecture 37

• The laws of thermodynamics
  ➢ Entropy
  ➢ Third law of thermodynamics

http://www.physics.wayne.edu/~apetrov/PHY2130/
Last lecture:

1. Thermodynamics
   ✓ Heat engines. Carnot cycle. $e_{Carnot} = 1 - \frac{|T_c|}{|T_h|}$

**Review Problem:** Your friend has constructed a heat engine that (as he claims) operates with 40% efficiency. The engine receives heat from the hot reservoir ($T_H = 400$ K) and expels heat to the cold reservoir ($T_C = 300$ K). Your friend is

1. telling the truth
2. not completely honest with you
3. saying something that you cannot possibly verify with the provided data.
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✓ 2. not completely honest with you

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Note: Maximally possible efficiency of a heat engine that operates in these conditions is that of a Carnot’s engine, i.e.

$$e_{\text{max}} = 1 - \frac{|T_c|}{|T_h|} = 1 - \frac{300K}{400K} = 0.25 \text{ or } 25\%$$

Thus, your friend should check his measurements.
Entropy

• A state variable related to the Second Law of Thermodynamics, the entropy

• The change in entropy, $\Delta S$, between two equilibrium states is given by the energy, $Q_r$, transferred along the reversible path divided by the absolute temperature, $T$, of the system in this interval
Entropy

Mathematically, \[ \Delta S = \frac{Q_r}{T} \]

This applies only to the reversible path, even if the system actually follows an irreversible path.

- To calculate the entropy for an irreversible process, model it as a reversible process.
- When energy is absorbed, \( Q \) is positive and entropy increases.
- When energy is expelled, \( Q \) is negative and entropy decreases.
More About Entropy

• Note, the equation defines the *change in entropy*

• The entropy of the Universe increases in all natural processes
  • This is another way of expressing the Second Law of Thermodynamics

• There are processes in which the entropy of a system decreases
  • If the entropy of one system, A, decreases it will be accompanied by the increase of entropy of another system, B.
  • The change in entropy in system B will be greater than that of system A.
The second law of thermodynamics (Entropy Statement):
The entropy of the universe never decreases.
Example: An ice cube at 0.0 °C is slowly melting. What is the change in the ice cube’s entropy for each 1.00 g of ice that melts?

To melt ice requires \( Q = mL_f \) joules of heat. To melt one gram of ice requires 333.7 J of energy.

The entropy change is

\[
\Delta S = \frac{Q}{T} = \frac{333.7 \text{ J}}{273 \text{ K}} = 1.22 \text{ J/K.}
\]
Perpetual Motion Machines

• A perpetual motion machine would operate continuously without input of energy and without any net increase in entropy

• Perpetual motion machines of the first type would violate the First Law, giving out more energy than was put into the machine

• Perpetual motion machines of the second type would violate the Second Law, possibly by no exhaust

• Perpetual motion machines will never be invented
Perpetual Motion Machines

Robert Fludd's 1618 "water screw" perpetual motion machine

The "Overbalanced Wheel"
Entropy and Disorder

- Entropy can be described in terms of disorder

- A disorderly arrangement is much more probable than an orderly one if the laws of nature are allowed to act without interference
  - This comes from a statistical mechanics development

Definition: A **microstate** specifies the state of each constituent particle in a thermodynamic system. A **macrostate** is determined by the values of the thermodynamic state variables.
### Possible Results of Tossing Four Coins

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>Microstates</th>
<th>Number of Microstates</th>
<th>Probability of Macrostate</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 heads</td>
<td>HHHH</td>
<td>1</td>
<td>$\frac{1}{16}$</td>
</tr>
<tr>
<td>3 heads</td>
<td>HHHT, HHTH, HTHH, THHH</td>
<td>4</td>
<td>$\frac{4}{16}$</td>
</tr>
<tr>
<td>2 heads</td>
<td>HHTT, HTHT, HTHH, THHT, THTH, TTHH</td>
<td>6</td>
<td>$\frac{6}{16}$</td>
</tr>
<tr>
<td>1 head</td>
<td>HTTT, THTT, TTHT, TTTT</td>
<td>4</td>
<td>$\frac{4}{16}$</td>
</tr>
<tr>
<td>0 heads</td>
<td>TTTT</td>
<td>1</td>
<td>$\frac{1}{16}$</td>
</tr>
</tbody>
</table>

Total number of microstates = 16

The probability of a macrostate is given by:

$$\text{probability of a macrostate} = \frac{\text{number of microstates corresponding to the macrostate}}{\text{total number of microstates for all possible macrostates}}$$
Entropy and Disorder

- Isolated systems tend toward greater disorder, and entropy is a measure of that disorder.

\[ S = k_B \ln \Omega \]

- \( k_B \) is Boltzmann’s constant.
- \( \Omega \) is a number proportional to the probability that the system has a particular configuration (the number of microstates).

- This gives the Second Law as a statement of “what is most probably” rather than “what must be”.

- The Second Law also defines the direction of time of all events as the direction in which the entropy of the universe increases.
Example: For a system composed of two identical dice, let the macrostate be defined as the sum of the numbers showing on the top faces. What is the maximum entropy of this system in units of Boltzmann’s constant?

<table>
<thead>
<tr>
<th>Sum</th>
<th>Possible microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(1,1)</td>
</tr>
<tr>
<td>3</td>
<td>(1,2); (2,1)</td>
</tr>
<tr>
<td>4</td>
<td>(1,3); (2,2); (3,1)</td>
</tr>
<tr>
<td>5</td>
<td>(1,4); (2,3); (3,2); (4,1)</td>
</tr>
<tr>
<td>6</td>
<td>(1,5); (2,4), (3,3); (4,2); (5,1)</td>
</tr>
<tr>
<td>7</td>
<td>(1,6); (2,5); (3,4), (4,3); (5,2); (6,1)</td>
</tr>
<tr>
<td>8</td>
<td>(2,6); (3,5); (4,4) (5,3); (6,2)</td>
</tr>
<tr>
<td>9</td>
<td>(3,6); (4,5); (5,4) (6,3)</td>
</tr>
<tr>
<td>10</td>
<td>(4,6); (5,5); (6,4)</td>
</tr>
<tr>
<td>11</td>
<td>(5,6); (6,5)</td>
</tr>
<tr>
<td>12</td>
<td>(6,6)</td>
</tr>
</tbody>
</table>
Example continued:

The maximum entropy corresponds to a sum of 7 on the dice. For this macrostate, $\Omega = 6$ with an entropy of

$$S = k \ln \Omega = k \ln 6 = 1.79k.$$
Heat Death of the Universe

- The entropy of the Universe always increases
- The entropy of the Universe should ultimately reach a maximum
  - At this time, the Universe will be at a state of uniform temperature and density
  - This state of perfect disorder implies no energy will be available for doing work
- This state is called the *heat death* of the Universe
The Third Law of Thermodynamics

It is impossible to cool a system to absolute zero.
Recall: Efficiency of a Carnot Engine

• Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs

\[ e_c = 1 - \frac{T_c}{T_h} \]

• Efficiency is 100% only if \( T_c = 0 \text{ K} \)
  • Such reservoirs are not available