Entropy

Carnot Cycle from last time, and 2nd law: "Heat to work itself"

Carnot is most efficient that we can get because it is reversible. \( \Rightarrow \) Run backwards as refrigerator

Suppose we had a more efficient engine. Couple it to a Carnot refrigerator.

\[
\begin{align*}
W &= Q_H + Q_C \\
E &= 1 + \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}
\end{align*}
\]

More eff \( \Rightarrow \) \( Q_H \rightarrow Q_H + \Delta \)

\( \frac{1}{2} W \rightarrow W + \Delta \)

Convert \( \Delta \) of heat into \( \Delta \) of work.

\( \Rightarrow \) Convert heat completely to work

which violates 2nd law of thermodynamics.
Why can't energy flow from cold to hot?

Entropy -- a measure of disorder.

Imagine the free expansion of a gas.

Initially, the molecules are all in one half.
Afterward, they are distributed throughout.

Is this reversible? No. But why not?
It could happen, but it doesn't.

Microscopically, we can describe the state of the system by specifying \( x_i \) and \( \bar{x}_i \) for each \( i \)th molecule. Of course there are a lot of them, so \( P, V, N, T \) is easier. (Macroscopic vs. microscopic.) But suppose we did. Let's make it 1D for simplicity.

Initially, \( x_i \leq 0 \) for all \( i \).

Finally, \( x_i > 0 \) and \( x_i < 0 \) are equally probable.
There is a 50/50 chance that the \( i \)th one is at \( x < 0 \).

What is the probability that all of them have \( x < 0 \)?

\[
\text{Prob} = \left( \frac{1}{2} \right)^N \approx \frac{1}{2^{10^{23}}} \quad \text{tiny!} \quad \text{but not zero!}
\]

System could happen to go back to initial "half full" state, but don't bet on it. It is as probable as flipping \( 10^{23} \) heads in a row. A random-even split is more likely.

But, you may protest, it is just as unlikely that we get

\[-+--+-++-+-+-++-\ldots\]

\[
\text{Prob} = \left( \frac{1}{2} \right)^N \quad \text{as well.}
\]

True, but I can switch the molecules around (e.g. \( ++--+++-\ldots \)) and have a microscopically distinct state that is macroscopically the same. Call this disordered because we don't know individual states. Disorder is more likely because there are more disordered states than ordered states.
The most probable macroscopic state is the one with the most corresponding microscopic states. That is also the one with the greatest disorder — the greatest entropy.

Entropy, $S = k \ln \omega$

- $\omega$: number of possible microscopic states for a macroscopic state
- $k$: Boltzmann's constant

All molecules on one side has $\omega = 1$. Only one way to do that $\Rightarrow S = 0$

Equal #s per side is much more likely, because there are more states.

Entropy is a property describing the whole system.

What is the entropy change in a free expansion from $V$ to $2V$?

Number of states increases: possible positions double for each molecule.
Total number of microscopic states increases by $2^n$.

\[ S_1 = k \ln w, \]
\[ S_2 = k \ln (2^n w), \]
\[ \Delta S = k \ln 2^n w - k \ln w = k \ln \frac{2^n w}{w}, \]
\[ = k \ln 2^n \]
\[ = k N \ln 2 \]
\[ = k n N_a \ln 2 \]
\[ x = \frac{R}{N_a} \]
\[ \Rightarrow \Delta S = n R \ln 2. \]

But, we really don't want to have to count molecules to calculate entropy. We want a macroscopic relation.

To do that, we need to start with reversible processes, then generalize later. (Note that a free expansion is not reversible.)
Entropy change for an infinitesimal, reversible process.

Let's try to accomplish the same thing as our $V \to 2V$ free expansion, but do it reversibly.

To a good approximation, an infinitesimal change in heat at constant $T$ is reversible:

$$dU = dQ - dW \quad \Rightarrow \quad dU = 0 \quad \text{if} \quad T \text{ constant}.$$  

$$dQ = dW \quad \Rightarrow \quad dQ = dW = p\,dV = \frac{nRT}{V} \, dV$$

$$ds = \frac{dQ}{T} = nR \frac{dV}{V}$$

$$S \Rightarrow \Delta S = nR \ln \frac{V_2}{V_1}$$

Note that $\Delta S=0$ for a cyclic reversible process like Carnot cycle. Most natural processes are not reversible, like free expansion.
Stated w/o proof...

\[ \Delta S \text{ between two states does not depend on the path used, just the starting \& ending states.} \]

So, to find \( \Delta S \) of a non-reversible process, we have to find a way between the two states which is reversible, i.e., isothermal or adiabatic.

E.g. Free expansion of a gas from \( V \) to \( 2V \). Some states as our isothermal heating.

\[ \Delta S = nR \ln \frac{2V}{V} = nR \ln 2. \]

E.g. Calculate \( \Delta S \) for 1 kg of water heated from 10°C to 20°C.

Treat it as slow -- infinitesimally -- so reversible.

\[ \Delta S = \int \frac{dQ}{T} = \int \frac{mc \, dT}{T} = mc \ln \frac{T_2}{T_1} \]

\[ = 1 \text{ kg} \cdot \frac{4190 \text{ J}}{\text{kg} \cdot \text{K}} \ln \frac{293}{283} = 4190 \times 0.035 \]

\[ = 145 \frac{\text{J}}{\text{K}} \]
Note that $\Delta S$ depends on temperatures. A $10^\circ$ change not same at higher $T$.

Second Law of Thermodynamics is

$$\Delta S \geq 0$$

for all natural processes on a complete system.

We saw $\Delta S = 0$ for reversible cycles.

$> 0$ for non-reversible.

But what about cooling something (e.g. from $20^\circ$ to $10^\circ$)?

We would find $\Delta S < 0$, see e.g. previous examples.

Why doesn't this violate the $2^\text{nd}$ law?

Because we have to consider the whole system. How do we cool it?

$$\Delta S = ? = m_1 c_1 \ln \left( \frac{T_f}{T_i} \right) + m_2 c_2 \ln \left( \frac{T_f}{T_2} \right)$$

$= \text{change in entropy of the whole system}$.
In this case, if both masses are the same,

\[ \Delta S = mc \left( \ln \frac{283}{293} + \ln \frac{283}{273} \right) \]

\[ = mc \left( \ln 0.966 + \ln 1.0366 \right) \]

\[ = mc \left( -0.0346 + 0.036 \right) \]

\[ = mc \times 1 \times 10^{-3} \]

\[ > 0. \]

Example: \( \Delta S \) for melting 1 kg of ice?

\[ \Delta S = \int_{1}^{2} \frac{dQ}{T} = \frac{1}{T} \int_{1}^{2} dQ = \frac{1}{T} \Delta Q \]

\[ \Delta Q = \frac{1 \text{ kg} \times \text{(Heat of fusion)}}{T} \]

\[ = \frac{1 \times (3.34 \times 10^5 \text{ J/kg})}{T} \]

\[ = \frac{3.34 \times 10^5}{273} = 1220 \text{ J/K} \]

\( \Delta S \) to show? \( = -1220 \) because reversible because it is at the same temperature.
Problem 16-17

Nebula with $T = 7500 \text{ K}$

80 molecules/cm$^3$. What is $P$?

$$P = \frac{nRT}{V} = \frac{N}{N_A} \frac{RT}{V} = \frac{80 \times 8.314 \times 7500}{6 \times 10^{23} (0.01)^3} = 8 \times 10^{-12} \text{ Pa}$$

So, if $T$ is so high, would your spaceship burn up in that nebula?

No. It is mostly $H_2$.

$\rightarrow$ $C_V \approx 20 \text{ J/mol K}$

80 molecules/cm$^3 \rightarrow 80 \times 10^6$ molecules/m$^3$

$\rightarrow 1 \times 10^{-16}$ moles/m$^3$

$\Rightarrow dQ = 10^{-16} \cdot 20 \frac{\text{J}}{\text{mol K}} \cdot (7500 - 300)$

$\Rightarrow dQ = 10^{-16} \cdot 10^5 = 10^{-11} \text{ J/m}^3$. 
Sample Problem:

Compressed air. You stand on an inner tube.

\[ \Delta U = Q - W \rightarrow -mg \Delta h \]

\[ \rightarrow nC_v \Delta T \text{ for an ideal gas.} \]

\[ \rightarrow = 0 \text{ for adiabatic} \]

\[ + mgh = nC_v (T_2 - T_1) \]

\[ T_2 - T_1 = \frac{mgh}{nC_v} = \frac{100 \cdot 10 \cdot 0.1}{1.3 \cdot 8.314} \approx 10^6 \text{ K} \]
Cloud Chamber

Rapid decompression: => Cloud Formation => Condensation

Clouds form around small impurities found that these are traces.

Cosmic rays

Mountain Rains:

Lower p: => cooler: => condense: => rain
Sample problem:

Three isothermal processes are shown for the same, ideal gas. They each have the same initial and final volumes, $V_i$ to $V_f$, but different temperatures.

d) Rank the processes according to the work done by the gas.

e) Rank by change in internal energy.

f) Rank by heat transferred to gas.

\[ dW = p \, dV = nRT \frac{dU}{V} \]
Sample Problem:

\[ B = m_{\text{air}} g - m_{\text{water}} g = (P_{\text{air}} - P_{\text{water}}) V g \]

\[ B = (P_{\text{air}} - P_{\text{water}}) V g \frac{x}{L} \]

\[ \Rightarrow \text{SHM} \quad \text{freq} = \frac{1}{2\pi} \omega = \frac{1}{2\pi} \]

\[ m \frac{x^2}{L^2} + (P_{\text{air}} - P_{\text{water}}) V \frac{g x}{L} = 0 \]

\[ \Rightarrow \omega = \sqrt{\frac{(P_{\text{air}} - P_{\text{water}}) V g}{m}} \]

But, it will be damped oscillation since under water.
Force on a dam

\[ p = p_0 + \rho g h = \rho g h \]

So, force on a small region \( dA \) at height \( y \) is

\[ dF = p \cdot dA = \rho g (H-y) \, dy \]

\[ F = \int_0^H \rho g (H-y) \, dy = \rho g \left[ H y - \frac{y^2}{2} \right]^H_0 \]

\[ = \rho g H^2 - \frac{1}{2} \rho g H^2 \]

\[ = \frac{1}{2} \rho g H^2 \]

\[ \rightarrow \text{quadratic with height, linear with width} \]

That is total force.

Force on a small area at the bottom depends only on \( H \).
Sample Problem

\[ \begin{array}{c|c|c|c}
\hline
\text{P}_2 & \text{h} & \delta P_1 \\
\hline
\text{g}_2 & \text{g}_1 & \\
\hline
\end{array} \rightarrow v_1 \]

What is \( v_1 \) velocity of ejected fluid?

At surface, \( \frac{1}{2} \) at spot, Bernoulli's equation is same.

\[ P_2 + \frac{1}{2} \rho v^2 + \rho g h = P_1 + \frac{1}{2} \rho v^2 + \rho g h. \]

\[ \frac{1}{2} \rho v^2 = (P_2 - P_1) + \rho g (h_2 - h_1). \]

\[ v^2 = 2 \frac{P_2 - P_1}{\rho} + 2 gh \]

\[ v = \sqrt{2 \frac{(P_2 - P_1)}{\rho} + 2 gh}. \]

Limits ok? \( P_2 - P_1 = 0 \Rightarrow \sqrt{2 gh} \quad \text{... just energy relation.} \)

\( g = 0 \Rightarrow P_2 < P_1 \)? \( v = \sqrt{-2 \frac{\rho}{g}} (P_2 - P_1) \quad ? \quad \text{Just negative v.} \)
How far does the fluid go before hitting the ground?

Just free-fall, so find time to fall then \( x = vt \).

\[-y_i = -\frac{1}{2} g t^2 \quad \Rightarrow \quad t = \sqrt{\frac{2y_i}{g}}\]

\[x = vt = \frac{\sqrt{2\left(P_2 - P_i\right)} + \frac{2gh}{g}}{f} \]

\[= \frac{\sqrt{4\left(P_2 - P_i\right) y_i}}{f} + \frac{4y_i h}{g}\]

\[= 2 \frac{\sqrt{\left(P_2 - P_i\right) y_i}}{f} + y_i h\]

If \(P_2 - P_i\), such as open container, then

\[x = 2 \sqrt{y_i h}\]
Freeze rate for a pond

In the winter, the water in a pond freezes beginning from the surface because ice floats. Over time, the ice thickens by extending toward the bottom of the pond. Suppose that a pond is freezing due to cold air above it. At what rate does the thickness of the ice increase, assuming that the temperature of the air stays constant at $T_{\text{air}}$?

Once a layer of ice forms, it insulates the water from the colder air above it. So, the rate of freezing is set by the rate at which heat conducts through the existing ice layer. As the ice gets thicker, it becomes a better insulator and slows the rate of freezing. To quantify this, imagine an area, $A$, of ice that has a thickness $y$. The heat flow rate from the air, through the ice, to the water is

$$\frac{dQ}{dt} = \frac{kA\Delta T}{y},$$

where $\Delta T = T_{\text{air}}$ since the water just below the ice is at $0^\circ \text{C}$. A quantity of heat, $\Delta Q$, freezes water with mass,

$$\Delta m = \Delta Q/L_F,$$

where $L_F$ is the latent heat of fusion, the heat required to melt a kilogram of ice. So the rate at which the mass increases is

$$\frac{dm}{dt} = \frac{1}{L_F} \frac{dQ}{dt} = \frac{kA\Delta T}{yL_F}.$$

We want the rate that the thickness increases. That can be found from the mass with $m = \rho_{\text{ice}}V$. So $dm/dt = \rho_{\text{ice}}dV/dt = \rho_{\text{ice}}Ady/dt$. Thus,

$$\frac{dy}{dt} = \frac{1}{\rho_{\text{ice}}A} \frac{dm}{dt} = \frac{kA\Delta T}{\rho_{\text{ice}}AyL_F} = \frac{k\Delta T}{\rho_{\text{ice}}yL_F}.$$

So,

$$\frac{dy}{dt} = \frac{kT_{\text{air}}}{\rho_{\text{ice}}yL_F}.$$

$$= \frac{(1.6 \text{ W/mK})}{(0.92 \times 10^3 \text{ kg/m}^3)} \left(\frac{334 \times 10^3 \text{ J/kg} \cdot {^\circ}\text{C}}{y^3}\right) \frac{T_{\text{air}}}{y} = 5 \times 10^{-9} \frac{T_{\text{air}}}{y}.$$

For 10 cm thick ice and $T_{\text{air}} = -5^\circ \text{C}$, $g = 0.3 \text{ m/s}^2$.

$$\approx 0.3 \text{ microns/sec}.$$

For $1 \text{ cm}$ thick ice and $T_{\text{air}} = -5^\circ \text{C}$, $g = 0.3 \text{ microns/sec}$.

$$\approx 3 \text{ cm per day}.$$