Lecture 13
Heat Engines

- Thermodynamic processes and entropy
- Thermodynamic cycles
- Extracting work from heat
  - How do we define engine efficiency?
  - Carnot cycle: the best possible efficiency

Reading for this Lecture:
Elements Ch 4D-E, 10A-B
Review

Entropy in Macroscopic Systems

Traditional thermodynamic entropy: \( S = k \ln \Omega = k\sigma \)

We want to calculate \( S \) from macrostate information (\( p, V, T, U, N, \text{ etc.} \)).

Start with the definition of temperature in terms of entropy:

\[
\frac{1}{kT} \equiv \left( \frac{\partial \sigma}{\partial U} \right)_{V,N}, \text{ or } \frac{1}{T} \equiv \left( \frac{\partial S}{\partial U} \right)_{V,N}
\]

The entropy changes when \( T \) changes: (We're keeping \( V \) and \( N \) fixed.)

\[
dS = \frac{dU}{T} = \frac{C_V dT}{T} \implies \Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T}
\]

If \( C_V \) is constant:

\[
= C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln \left( \frac{T_2}{T_1} \right)
\]
When V is constant: \( dS \equiv dU/T = dQ/T \) \( \iff W = 0, \text{ so } dU = dQ \)

In fact, \( dS = dQ/T \) during any reversible (quasi-static) process, even if V changes.

The reason: In a reversible process, \( S_{\text{tot}} \) (system plus environment) doesn’t change:

\[
0 = dS_{\text{sys}} + dS_E \quad \Delta S_{\text{tot}} = 0 \text{ if process is reversible.}
\]

\[
= dS_{\text{sys}} + \frac{dU_E}{T} \quad \text{The reservoir is supplying (or absorbing) heat.}
\]

\[
= dS_{\text{sys}} - \frac{dQ}{T} \quad \text{The reservoir’s energy gain is the system’s heat loss.}
\]

That’s how they interact.

\[
dS = \frac{dQ}{T}, \quad \text{or } \Delta S = \int_{\text{init}}^{\text{final}} \frac{dQ}{T}
\]

for any reversible process
ΔS in Isothermal Processes

Suppose V & p change but T doesn’t.

Work is done (dW_{by} = pdV).
Heat must enter to keep T constant: \( dQ = dU + dW_{by} \).

So:

\[
\frac{dS}{T} = \frac{dU + dW_{by}}{T} = \frac{dU + pdV}{T}
\]

Special case, ideal gas:
For an ideal gas, if dT = 0, then dU = 0.

\[
dS = \frac{\rho dV}{T} = \frac{NkTdV}{VT} = \frac{NkdV}{V}
\]

\[
\Delta S = \int_{V_1}^{V_2} \frac{NkdV}{V} = Nk \ln \left( \frac{V_2}{V_1} \right)
\]

Remember: This holds for quasi-static processes, in which the system remains near thermal equilibrium at all times.
1) The entropy of a gas increases during a quasi-static isothermal expansion. What happens to the entropy of the environment?
   a) $\Delta S_{\text{env}} < 0$  
   b) $\Delta S_{\text{env}} = 0$  
   c) $\Delta S_{\text{env}} > 0$

2) Consider instead the ‘free’ expansion (i.e., not quasi-static) of a gas. What happens to the total entropy during this process?
   a) $\Delta S_{\text{tot}} < 0$  
   b) $\Delta S_{\text{tot}} = 0$  
   c) $\Delta S_{\text{tot}} > 0$
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Energy (heat) leaves the environment, so its entropy decreases. In fact, since the environment and gas have the same T, the two entropy changes cancel: $\Delta S_{\text{tot}} = 0$. This is a reversible process.

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There is no work or heat flow, so $U_{\text{gas}}$ is constant. $\Rightarrow T$ is constant. However, because the volume increases, so does the number of available states, and therefore $S_{\text{gas}}$ increases. Nothing is happening to the environment. Therefore $\Delta S_{\text{tot}} > 0$. This is not a reversible process.
Q = 0 (definition of an adiabatic process)
V and T both change as the applied pressure changes.
For example, if p increases (compress the system):
• V decreases, and the associated S also decreases.
• T increases, and the associated S also increases.
These two effects must exactly cancel!!
Why? Because:
• This is a reversible process, so $S_{tot} = 0$.
• No other entropy is changing.
  (Q = 0, and $W_{by}$ just moves the piston.)

So, in a quasi-static adiabatic process, $\Delta S = 0$.

Note: We did not assume that the system is an ideal gas. This is a general result.
Entropy-increasing processes are irreversible, because the reverse processes would reduce entropy.

Examples:
- Free-expansion (actually, any particle flow between regions of different density)
- Heat flow between two systems with different temperatures.

Consider the four processes of interest here:
- Isothermal: Heat flow but no $T$ difference. Reversible
- Adiabatic: $Q = 0$. No heat flow at all. Reversible
- Isochoric & Isobaric: Heat flow between different $T$’s. Irreversible
  (Assuming that there are only two reservoirs.)
Two blocks, each with heat capacity* $C = 1 \text{ J/K}$ are initially at different temperatures, $T_1 = 250 \text{ K}$, $T_2 = 350 \text{ K}$. They are then placed into contact, and eventually reach a final temperature of 300 K. (Why?) What can you say about the total change in entropy $\Delta S_{\text{tot}}$?

a) $\Delta S_{\text{tot}} < 0$  
b) $\Delta S_{\text{tot}} = 0$  
c) $\Delta S_{\text{tot}} > 0$

*For a solid, $C = C_V = C_p$, to good approximation, since $\Delta V \approx 0.$
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- a) \( \Delta S_{\text{tot}} < 0 \)
- b) \( \Delta S_{\text{tot}} = 0 \)
- c) \( \Delta S_{\text{tot}} > 0 \)

This is an irreversible process, so there must be a net increase in entropy. Let’s calculate \( \Delta S \):

\[
\Delta S_{\text{tot}} = C \ln \left( \frac{T_f}{T_1} \right) + C \ln \left( \frac{T_f}{T_2} \right)
\]

\[
= C \ln \left( \frac{300}{250} \right) + C \ln \left( \frac{300}{350} \right)
\]

The positive term is slightly bigger than the negative term.

\[
= C \ln \left( \frac{300^2}{250 \times 350} \right) = (0.028)C = 0.028 \text{ J/K}
\]

*For a solid, \( C = C_V = C_p \), to good approximation, because \( \Delta V \approx 0 \).
We will assume ideal gases in our treatment of heat engines, because that simplifies the calculations.

**Isochoric (constant volume)**

\[
W_{by} = \int p \, dV = 0
\]

\[
\Delta U = \alpha N k \Delta T = \alpha V \Delta p
\]

\[
Q = \Delta U
\]

**Isobaric (constant pressure)**

\[
W_{by} = \int p \, dV = p \Delta V
\]

\[
\Delta U = \alpha N k \Delta T = \alpha p \Delta V
\]

\[
Q = \Delta U + W_{by} = (\alpha + 1) p \Delta V
\]
Review (2)

Isothermal (constant temperature)

$$ W_{by} = \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \frac{NkT}{V} \, dV = NkT \ln \left( \frac{V_2}{V_1} \right) $$

$$ \Delta U = 0 $$

$$ Q = W_{by} $$

Adiabatic (no heat flow)

$$ W_{by} = - \Delta U $$

$$ \Delta U = \alpha Nk (T_2 - T_1) = \alpha (p_2V_2 - p_1V_1) $$

$$ Q = 0 $$
A closed cycle is one in which the system returns to the initial state. (same $p$, $V$, and $T$) For example:

- $U$ is a state function. Therefore: $\Delta U = 0$
- The net work is the enclosed area: $W = \oint pdV \neq 0$
- Energy is conserved (1st Law): $Q = \dot{W} \neq 0$

Though of course we could use any curves to make a closed cycle, here we will consider isochoric, isobaric, isothermal, and adiabatic processes.
Introduction to Heat Engines

One of the primary applications of thermodynamics is to Turn heat into work.

The standard heat engine works on a cyclic process:

1) extract heat from a hot reservoir,
2) perform work, using some of the extracted heat,
3) dump unused heat into a cold reservoir (often the environment).
4) repeat over and over. We represent this process with a diagram:

A “reservoir” is a large body whose temperature doesn’t change when it absorbs or gives up heat.

For heat engines we will define $Q_h$, $Q_c$, and $W_{by}$ as positive.

Energy is conserved: $Q_h = Q_c + W_{by}$
Two reservoirs: $T_h$ and $T_c$.
Four processes: Two isotherms and two isochors
The net work during one cycle: The area of the “parallelogram”.
Which processes in a Stirling cycle correspond to $Q_h$ in the heat flow diagram?

a) 1
b) 2
c) 1 and 2
d) 3
e) 3 and 4
Solution

Which processes in a Stirling cycle correspond to $Q_h$ in the heat flow diagram?

a) 1
b) 2
\[ \boxed{\textbf{c) 1 and 2}} \]
d) 3
e) 3 and 4

Process 1 is obvious, since we’re heating the gas. In the isothermal expansion (process 2), although the temperature is kept constant we still have to put heat in to do the work from the expansion.
The Stirling Cycle (2)

1) Isochoric
Gas temperature increases at constant volume (piston can't move)

2) Isothermal
Gas expands at constant $T_h$

3) Isochoric
Gas temperature decreases at constant volume (piston can't move)

4) Isothermal
Gas is compressed at constant $T_c$

The cycle goes around like this. We don't describe the mechanical parts that move the gas cylinder back and forth between the reservoirs.
How Does this Engine Do Work?

Look at the two isothermal processes (2 and 4) on the previous slide:
- **Process 2**: expanding gas does $W_2$ on the piston, as it expands from $V_a$ to $V_b$.
- **Process 4**: contracting gas is done $W_4$ by the piston, as it contracts from $V_b$ to $V_a$.

If $W_2 > W_4$, the net work is positive.
This is true, because the contracting gas is colder ($\Rightarrow$ lower pressure).

During one cycle:
- The hot reservoir has lost some energy ($Q_h = Q_{h1} + Q_{h2}$).
- The cold reservoir has gained some energy ($Q_c = Q_{c3} + Q_{c4}$).
- The engine (the gas cylinder) has neither gained nor lost energy.

The energy to do work comes from the hot reservoir, not from the engine itself.

The net work done by the engine is:

$$W_{by} = W_2 - W_4 = Q_h - Q_c = Q_{h2} - Q_{c4}$$

Not all of the energy taken from the hot reservoir becomes useful work. Some is lost into the cold reservoir. We would like to make $Q_c$ as small as possible.
Heat Engine Efficiency

We pay for the heat input, $Q_h$, so:

Define the efficiency

$$\varepsilon = \frac{\text{work done by the engine}}{\text{heat extracted from reservoir}} = \frac{\text{results}}{\text{cost}}$$

$$\varepsilon \equiv \frac{W_{by}}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Valid for all heat engines. (Conservation of energy)

Cartoon picture of a heat engine:

Hot reservoir at $T_h$

Engine

Cold reservoir at $T_c$

What’s the best we can do?

The Second Law will tell us.
The 2nd Law Sets the Maximum Efficiency (1)

\[ \Delta S_{\text{tot}} \geq 0 \]

How to calculate \( \Delta S_{\text{tot}} \)?

Over one cycle:

\[ \Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = 0 \]

Remember:

- \( Q_h \) is the heat taken from the hot reservoir, so \( \Delta S_{\text{hot}} = -\frac{Q_h}{T_h} \).
- \( Q_c \) is the heat added to the cold reservoir, so \( \Delta S_{\text{cold}} = +\frac{Q_c}{T_c} \).

From the definition of \( T \):

\[ \Delta S_{\text{hot}} = -\frac{Q_h}{T_h}, \quad \Delta S_{\text{cold}} = +\frac{Q_c}{T_c}. \]

\[ \Delta S_{\text{tot}} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0 \quad \text{2nd Law} \]

\[ \frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \]

\( Q_c \) cannot be zero. Some energy is always lost.
The 2\textsuperscript{nd} Law Sets the Maximum Efficiency (2)

efficiency \equiv \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}

\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \quad \text{from the 2\textsuperscript{nd} Law}

\Rightarrow \varepsilon \leq 1 - \frac{T_C}{T_H}

This is a universal law!! (equivalent to the 2\textsuperscript{nd} law)

It is valid for any procedure that converts thermal energy into work. We did not assume any special properties (e.g., ideal gas) of the material in the derivation.

The maximum possible efficiency, $\varepsilon_{\text{Carnot}} = 1 - \frac{T_C}{T_h}$, is called the Carnot efficiency. The statement that heat engines have a maximum efficiency was the first expression of the 2\textsuperscript{nd} law, by Sadi Carnot in 1824.
How Efficient Can an Engine be?

Consider an engine that uses steam ($T_h = 100\,^\circ\,C$) as the hot reservoir and ice ($T_c = 0\,^\circ\,C$) as the cold reservoir. How efficient can this engine be?

The Carnot efficiency is

$$\varepsilon_{\text{Carnot}} = 1 - \frac{T_c}{T_H} = 1 - \frac{273\,K}{373\,K} = 0.27$$

Therefore, an engine that operates between these two temperatures can, at best, turn only 27% of the steam’s heat energy into useful work.

Question: How might we design an engine that has higher efficiency?

Answer: By increasing $T_h$. (That’s more practical than lowering $T_c$.)

Electrical power plants and race cars obtain better performance by operating at a much higher $T_h$. 
When Is $\varepsilon$ Less than $\varepsilon_{\text{Carnot}}$?

We can write the efficiency loss in terms of the change of total entropy:

$$\Delta S_{\text{tot}} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = -\frac{Q_H}{T_H} + \frac{Q_H - W}{T_C}$$

$$\Rightarrow W = Q_H \left(1 - \frac{T_C}{T_H}\right) - T_C \Delta S_{\text{tot}}$$

$$\varepsilon \equiv \frac{W}{Q_H} = \left(1 - \frac{T_C}{T_H}\right) - \frac{T_C \Delta S_{\text{tot}}}{Q_H}$$

Lesson: Avoid irreversible processes. (ones that increase $S_{\text{tot}}$).
- direct heat flow from hot to cold
- free expansion (far from equilibrium)
- sliding friction
Next Time

Carnot Engines
Refrigerators
Heat Pumps