Theo. 4. Statistical Physics.
Lecture 4.
Felix Yu
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Last time: 1st law of thermodynamics, path independence
Extensive & intensive variables

Today: 2nd law of thermodynamics
Cycles & engines.
Carnot engine

From last time, we emphasized that trajectories in the state function could be adiabatic, such that the system only gained or lost energy because of work performed on or by the system, respectively.

We will now consider the overall interplay of heat, work, and cycles as reflected by the adiabatic + non-adiabatic processes.

In the context of trajectories, we have a few different possibilities for how a system affects change in its environment.

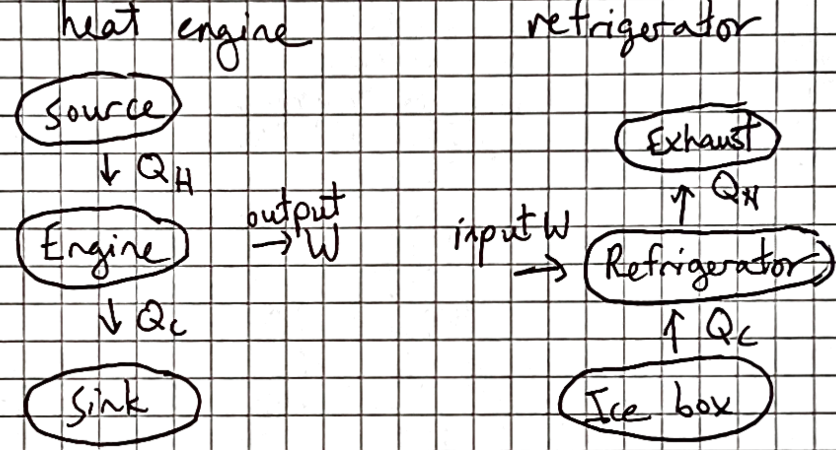
Heat engine: Takes some heat Q_H, converts a portion to work W, then dumps remaining heat Q_C to a heat sink / reservoir (like the atmosphere). The efficiency is defined as the net work fraction extracted from the heat energy, $\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1$.

In contrast, a refrigerator takes heat energy Q_c from a cold system and uses work W to dump the energy Q_H at a higher temperature:

$$\hat{\eta} = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_c}.$$

[Aside: W is in the denominator since removing Q_c amount of heat requires $W \geq Q_c$.]

Cartoons:



From the 1st law of thermodynamics, we cannot have a perpetual motion machine of the first kind, i.e. a machine that produces work but consumes no energy.

This is a consequence of the fact that a completely adiabatic cycle in thermodynamic coordinates would leave the system at the same initial & final energy, but by the first law, the work done on or by the system must then be zero.

We now formulate the second law of thermodynamics, which has two equivalent formulations:

Kelvin's statement: No process is possible whose sole result is the complete conversion of heat into work.

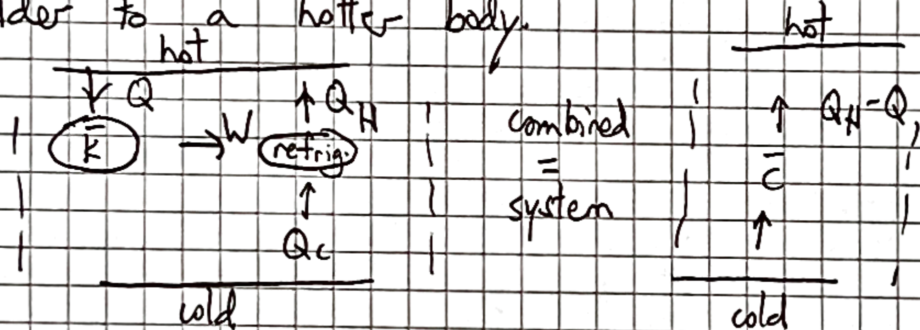
Clausius's statement: No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

In other words, a perfect heat engine & a perfect refrigerator are both forbidden. These statements forbid a perpetual machine of the second kind, meaning an engine that produces work by converting water into ice. Naturally, heat flows from hot objects into cold objects, but if such processes were perfectly efficient in transferring heat into work, then we would be able to perfectly store work energy in heat, which is not allowed.

We can show the two statements by Kelvin & Claudius are equivalent:

① Start with a machine violating Clausius's statement, which takes heat Q from cold to a hot region. We construct an engine to take heat Q_H in, expel Q_C out, and perform work $Q_H - Q_C$. In tandem, the hypothetical machine and the realistic engine would take $Q_H - Q$ from the hot source, produce work $Q_H - Q_c$, and expel $Q_c - Q$ into the cold reservoir. We can consider an engine for the special case of $Q_c = Q$, in which case the combined system takes $Q_H - Q_c$ from the hot source + performs $Q_H - Q_c$ work + expels no heat, which violates Kelvin's statement (+ the 2nd law).

Equivalently, we can show a machine that violates Kelvin's state can be used to run a refrigerator that only transfers heat from a colder to a hotter body.



So, the 2nd law of thermodynamics dramatically constrains the physical impact of closed loops in state functions (and more generally, non-equilibrium systems). Not only are adiabatic closed loops not useful in producing work, closed loops that include heat transfer always result in less than-perfect conversion of work energy into heat + vice versa.

It is natural to ask, what kind of closed cycle of trajectories gives the most optimal efficient engine? Given that engines are used in everyday life to perform work (converting internal energy into mechanical work), the answer to this question is profoundly important to understanding/maximizing efficiency & minimizing losses.

Ingredients:

We would want to minimize heat loss to the environment, so we should employ a trajectory that is quasi-static $\Rightarrow$ every point along the trajectory is in equilibrium, & is thus labeled by thermodynamic coordinates.

The first type of trajectory is adiabatic processes, but we know a closed loop using adiabatic processes only produces no work.

The second type of trajectory is an isotherm: given that we are trying to convert heat energy into work, we assume the existence of a heat source at T_H and a cold sink at T_C. Coupling our system to the heat source or cold sink lets us change the state function (internal energy) of the system in such a way as to displace the useful (and cancelling parts of the) trajectory characterized by adiabaticity.

Carnot's theorem.

We will now make the claim that a cycle constructed in such a way, which is called a Carnot engine, is the most efficient / ideal engine for extracting heat energy between two reservoirs.

Importantly, a Carnot engine is reversible since all trajectories are quasi-static.

Explicitly, we can consider a Carnot engine for the system of an ideal gas.

From the kinetic theory of gases, the internal kinetic energy $U = \frac{3}{2} N k_B T = \frac{3}{2} PV$ for a monatomic gas. (Will review next time)

Then, for a quasi-static path

$$đQ = dU - đW = d\left(\frac{3}{2} PV\right) + PdV$$
$$= \frac{5}{2} PdV + \frac{3}{2} VdP$$

The adiabaticity requirement is $đQ = 0$, and so a monatomic gas has adiabatic trajectories $5PdV + 3VdP = 0$

We get $\frac{5}{3}\frac{dV}{V} + \frac{dP}{P} = 0$

$$\frac{5}{3}\frac{dV}{V} = -\frac{dP}{P}$$

$$\frac{5}{3}\ln V = -\ln P + C_1$$

$$V^{5/3} = \frac{1}{P}\cdot C_2$$

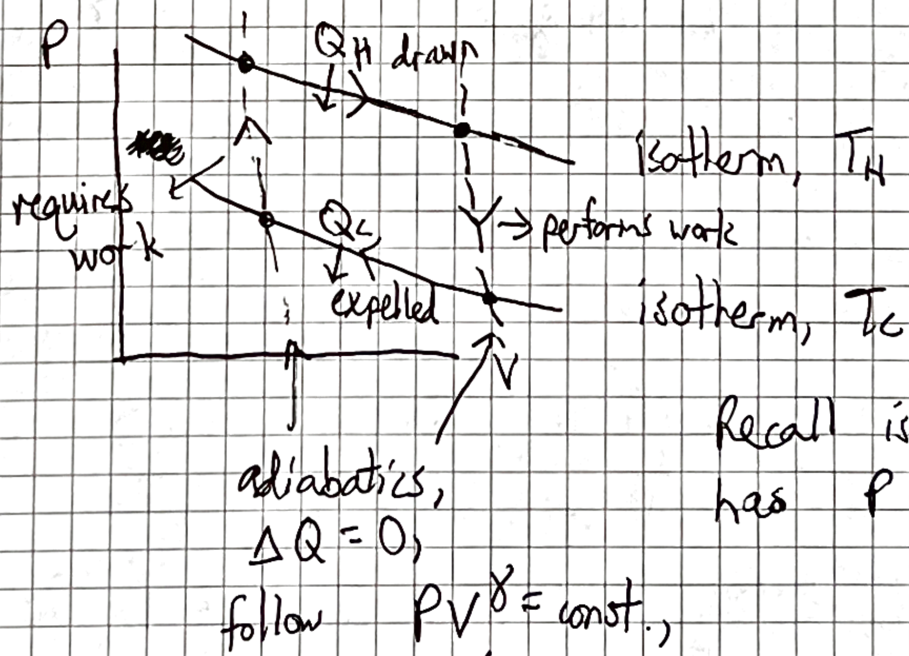
$$PV^{5/3} = \text{Const.}$$

Monatomic gases only have translational dofs; each dof contributes $\frac{1}{2}k_B T$ to energy.

The 5/3 power is usually denoted γ = adiabatic index.

For a diatomic gas, the possibility of additional rotational dof. gives $\frac{7}{5} = \gamma$ or additional rotational + vibrational dof gives $\frac{9}{7} = \gamma$.

So, we can draw a Carnot cycle in the (V, P) plane as:



Recall isotherm has $P \propto \frac{1}{V}$

We will analyze the efficiency of the Carnot engine next time.