Lecture 4 and 5. The Second Law

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Here we use the second law of thermodynamics to determine the efficiency of a simple heat engine. This will be useful in itself, and also allow us to define the a new state function, the entropy.

**Simple Heat Engine**

Consider a simple heat engine operating between two temperatures $T_1$ and $T_2$. We assume that all the heat transfer occurs from reservoirs located at these two fixed temperatures, and our engine draws heat from them (thus the system consists of 2 heat reservoirs and the engine). Clearly, this is a simplification of a real engine which may transfer heat over a wide range of temperatures; but the simple setup is easier to analyze and has a remarkable simple solution. The case of a more realistic engine is considered later. We also assume that our engine completes a cycle and returns to its initial state, and in the process it draws heat $Q_1$ from $T_1$ and rejects heat $Q_2$ from $T_2$. From energy conservation this cyclic process must do work $= Q_1 - Q_2$. We can define the efficiency of such a simple engine as the ratio of the heat input (in this case $Q_1$) to the work extracted $\eta = (Q_1 - Q_2)/Q_1$.

From the Second law of thermodynamics, we can make several statements about the efficiency of such simple engines.

1. For a given pair of temperatures $T_1$, $T_2$, the maximum efficiency is attained by a reversible engine.

2. All reversible engines have exactly the same efficiency. This efficiency is only a function of the two temperatures.

3. The efficiency of reversible simple heat engines can be used to define an absolute scale of temperature.

These statements are proved by combining different heat engines and utilizing the fact that a reversible process can be run in either direction. By such suitable constructions and using the Kelvin statement of the Second law of thermodynamics, the statements above can be established (eg. see *Feynman Lectures on Physics, Vol I, Chapter 44*).

A physical realization of the simple heat engine that operates in a reversible fashion is the Carnot engine. Here, a substance (eg a gas) with initial state at
temperature $T_1$ is heated isothermally, absorbing heat $Q_1$ at temperature the constant temperature $T_1$. Then, in order to reversibly transfer heat to the second reservoir, the system is thermally isolated and expanded (adiabatic expansion) till it attains the temperature $T_2$. Of course no heat is transferred during this process. Now, a certain amount of heat $Q_2$ can be transferred isothermally to the reservoir at temperature $T_2$, the amount being adjusted so that the system can return to its initial state via a final step, which is again an adiabatic process that compresses the fluid and returns it to initial temperature $T_1$. Throughout we assume there is no friction, and the changes are made slowly enough that the whole process is reversible. Since all reversible engines operating between a fixed pair of temperatures $T_1, T_2$ have the same efficiency, one can calculate the efficiency of a Carnot cycle using an ideal gas, where it is found to be

$$\eta = 1 - \frac{T_2}{T_1}$$

Here the ideal gas scale of temperature is used, coincides with the absolute definition of temperature that the efficiency of engines provides.

**Clausius Theorem**

Consider a general cyclic process. [This process need not be reversible or even quasi static (a quasi static process is always close to an equilibrium state of the system). Its intermediate states can be very far from equilibrium and not have well defined thermodynamic variables like temperature, pressure etc. All that is required is that the initial and final states of the cycle are the same equilibrium state.] During the course of this process heat $\{\Delta Q_1, \Delta Q_2 \ldots \Delta Q_i\}$ is transferred to this system from a heat source at temperatures $T_1, T_2, \ldots T_i$. The Clausius theorem states that:

$$\sum_i \frac{\Delta Q_i}{T_i} \leq 0$$

This is proved by considering a situation where the heat transfer to the system is accomplished by using a Carnot engine (although one does not have to heat every object this way, it is certainly possible and will lead to an important constraint.) The Carnot engine is assumed to have a high temperature reservoir at $T_0 > T_i$ and executes a cycle down to each of the temperatures $T_i$, delivering exactly the required quantities of heat $\Delta Q_i$. From the efficiency of Carnot engines we know that this implies a net amount of heat

$$\Delta Q' = T_0 \sum_i \frac{\Delta Q_i}{T_i} \leq 0$$

is absorbed from the heat reservoir at temperature $T_0$. Since both the system and the Carnot engine have gone through closed cycles, this heat is not stored as internal energy. Thus, by conservation of energy it must all have been converted into work done by the system and the engine. Therefore we have that the work
done by the system+engine is $\Delta W = \Delta Q'$. Now, since there is no other change in our system (everything else went through a cyclic process) heat cannot be converted into work. The only way is if $\Delta W \leq 0$. Since the temperature $T_0$ is positive, this yields the Clausius theorem for us.

The equality is obeyed for reversible processes.

$$\oint \frac{dQ}{T} = 0$$

**Entropy**

This allows us to define a state function, the entropy $S$. If we fix the entropy at some particular point $O$ to be $S_O$, then the entropy at point $A$ is given by:

$$S(A) = S_O + \int_O^A \frac{dQ}{T}$$

where the integral is taken along a reversible path. The fact that the integral vanishes over a closed reversible path implies that the entropy defined above is independent of path, so long as it is reversible. Thus, it is an property of the state of the system -once the entropy at point $O$ is fixed, we can find the entropy at any other point by connecting it to $O$ by a reversible process and measuring the heat delivered as a function of temperature and evaluating the integral above. Thus, although we appeal to reversible processes in order to define the entropy of a state, once we have shown that it is a property of the state, it does not matter how the system was prepared; it will always have the same entropy. In differential form the entropy is defined, along an infinitesimal reversible trajectory as:

$$TdS = \tilde{dQ}$$

Later we will see that the third law of thermodynamics fixes that arbitrary constant $S_O$ for us. It also allows us to define the relative entropy between two states that may not be easily connected by a reversible process, but can be connected via irreversible processes.

See K. Huang page 14-19 for more details.

It may be easily shown from the definition of entropy that reversible processes do not change the net entropy of the world (system plus heat baths) whereas irreversible processes inevitably increase the entropy of the world.

A useful way of thinking about entropy is the following. Consider a system at temperature $T$ connected to a heat bath. If it undergoes a change that results in a change in entropy $\Delta S$, this implies an opportunity to extrach heat $T\Delta S$ from the reservoir and convert it into work. In this way we do not change the entropy of the world, because the decrease in entropy of the heat bath is accounted for by the increase in entropy of the system. However, if this opportunity of extracting heat and converting it into work is not taken, then the entropy of the world increases, and the process becomes irreversible.
Another useful observation is the following. We know that energy can be transferred to an object by doing work on it, which is described by generalized coordinates and forces \( \bar{d}W = fdx \), eg \( \bar{d}W = -PdV \). But, energy can also be transferred in the form of disordered atomic motion. It turns out that the coordinate describing energy transfer of this kind is entropy, and the generalized force is temperature \( \bar{d}Q = TdS \).