Lecture 3: Thermodynamics - Reversible and Irreversible Processes.

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Although the microscopic laws governing the motion of atoms may be the same running forward or backwards in time (for example if you were shown a video of two billiard balls colliding elastically, it would look equally physical if it were shown to you running in reverse); when it comes to thermodynamic properties, a marked asymmetry under time reversal appears. For example, if you drop a stone, the initial energy can be converted into heating the stone; but one does not expect the reverse - i.e. heating the stone and it spontaneously flying up to the ceiling, and cooling at the same time. Similarly, while we expect heat energy to be transferred from a hot to a cold object spontaneously, the reverse is not true. In order to formalize these observations of the impossibility of certain transformations (although they obey the first law) one introduces the Second Law of Thermodynamics:

'There exists no thermodynamic transformation whose sole effect is to take heat and convert it into work.'

The crucial aspect here is that this cannot be the sole effect of the transformation. For example a hot gas can lift a weight placed on it and cool at the same time. Thus work has been extracted, but this was not the sole effect of the transformation, since the final state of the gas is different from the initial state. Note, that the reverse, solely converting work into heat, is certainly possible for example by using the rotating paddle wheel setup we discussed before in the context of the first law.

Sometimes the Second Law is stated differently, in terms of the impossibility of solely taking heat from a low temperature object and giving it up to a higher temperature object; but it can be shown that this is equivalent to the above statement (see Huang page 9,10). Thus the Second Law tells us that some processes run only one way. Actually, the fact that thermodynamics has such irreversibility built into it was already used by us very early on, while introducing the concept of equilibrium. The equilibrium state is obtained when we wait for a long time - clearly this implies a directionality in time (equilibrium states are not expected to spontaneously develop non-equilibrium character, which is the time reversed situation, at least within thermodynamics). Later, statistical
mechanics will provide a justification for the second law. It will be regarded as being true in a statistical sense, that it, is conceivably violated, but the chances for that to occur are so exceedingly small that we may discount it.

While some processes run only one way, it is also possible to construct processes that are reversible, and can run in both directions. A more quantitative criterion for reversibility will become available once we introduce the entropy. However, for the present we note the conditions under which reversibility can be achieved. To do this let us examine the situations in which irreversibility occurs. One example we have seen is if work is converted into heat, (since the reverse is not possible). This involves friction of some kind. Hence to construct a reversible process we need to eliminate friction between the moving parts of our system (or in the case of an electrical system, eliminate resistance to current flow). The other source of irreversibility we have already mentioned, is if a non equilibrium state is allowed to relax to equilibrium. This occurs for example if the volume of a gas is suddenly doubled - this is a highly nonequilibrium state since all the gas molecules are initially in one half of the container. The final equilibrium state contains a uniform distribution of gas in the container. Another example is the transfer of heat from a body at temperature $T_1$ directly to a colder body at temperature $T_2$, $T_2 < T_1$. Again a highly nonequilibrium state is attempting to relax to a distant equilibrium state. In order to eliminate irreversibility arising from such processes, we should consider changing the system smoothly and slowly (on a timescale over which it establishes equilibrium). In this way the system is never far from equilibrium, and a reversible process can result in the absence of friction. Note, that some changes, although slow, may result in irreversibility. Consider again the irreversible free expansion of a gas into a larger volume. If this is done in small increments, where the gas expands into successive small volumes repeatedly until it fills the entire volume then the process may appear ‘slow’ but it is nevertheless irreversible since each individual step is irreversible. Reversible expansion is obtained if we imagine applying on the piston a pressure just a little bit smaller than the pressure of the gas, that will make it move outwards slowly, in the absence of friction. Then, if we want to reverse the expansion we simply increase the pressure on the piston so it is infinitesimally above the internal pressure of the gas. Similarly, if we want to transfer heat in a reversible manner, we consider placing a reservoir of heat at a temperature just infinitesimally above the temperature of the body and then we can reverse the direction of heat flow by lowering the temperature of the reservoir infinitesimally. A more complete criterion for reversibility will be shortly available once we define entropy.