Sept. 25 2002: Lecture 9: ____________

Quasistatic Processes

Last Time

Forms of Work

Elastic Solids: Stress and Strain

Fluids: Pressure and Volume

PV work
Reversibility

Recall that we showed that the work performed cannot be a state function because:

$$\int dw = -\int PdV \neq 0 \quad (9-1)$$

Question: Why does the inequality in Eq. 9-1 show that the integral of \(dw\) is path dependent?

The differential work \(dw\) is sometimes called “not a perfect differential” because of this property. It simply means that you need even more information to integrate it—namely the path: \(\int dw\) is “path dependent”.

Furthermore, the idealization in Figure 8-1 is a somewhat misleading.

It is easy to specify what the volume is in such a system, but what about the pressure, \(P\), just after the beginning of the “spark” as the system expands rapidly? The pressure is not uniform and cannot be represented for the system by a point—so the curve cannot be represented by a series of points.
The idealization in Figure 8-1 introduces the topic of reversibility. (Sometimes, the terms quasi-equilibrium or quasi-static are used, they are effectively synonyms for reversible processes).

To illustrate what is meant by reversibility, consider the following simple processes:

Figure 9-2: An adiabatic processes consisting of an ideal fluid, a piston, and a mechanism for storing potential energy.
Figure 9-3: Case 1: A wasteful little demon removes all the weight at once. The system does no work because there is no force resisting the piston as it slides up the cylinder.

Figure 9-4: Case 2: A somewhat informed little demon removes the upper half of the weight. The system does some positive work as it lifts half the equilibrium force up.
Figure 9-5: Limiting (Reversible) Case: Slice weight into sheets $dx_i$ thick, where each $dx_i$ is picked so that the piston moves a constant distance after each removal of the weight. Each little volume of weight is stacked on the uniformly spaced shelf on the right by our extremely clever little demon. By induction, this will yield the most work. Work is maximized when reversible, but infinitely slow in this limit.

Question: Why is the word “reversible” applied to the case in Figure 9-5?

Therefore, the curves in Figure 8-1 are idealizations of a sequence of equilibrium states $(P, V)$. This idealization is called “quasi-static” and applies only if the system is changing very slowly. A quasi-static process is also called “reversible.”

Because $U$ is a state function, then it must be true in general that

$$\oint dU = 0 = \oint dq + \oint dw = \oint (dw + dq)$$

(9-2)

Because $dw$ depends on the path, so must $dq$; it is also not a perfect differential.
Heat Capacities

The fact that $dq$ is not a perfect differential is reflected by the observation that the heat capacity depends on path as well.

\[
    dq = C_V dT \quad \text{(constant volume)} \tag{9-3}
\]

\[
    dq = C_P dT \quad \text{(constant pressure)} \tag{9-4}
\]

$C_V$ is the heat capacity at constant $V$. $C_P$ is the heat capacity at constant $P$.

**Question:** In materials that expand while heating, they differ considerably. **Question:** which one should be bigger? **Why?**

For larger thermal expansion, the difference in heat capacities will be greater.

Gases, which expand considerably with temperature, have a large difference in their heat capacities.

Liquids do not expand as much. For $\text{H}_2\text{O}$ at $15^\circ\text{C}$ and $P = 1 \text{ atm}$, $c_p = 1\text{cal}/(\text{°K}\text{gram})$. (Note use of little $c$ for the derived intensive quantity on a per mass basis), and $c_V$ is only slightly different.

For solids, the difference is very small and usually neglected.