Recitation 2

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Introduction to Classical Thermodynamics

- Ordinary macroscopic material systems composed of a huge number of microscopic sub-components (atoms). 10^{23} particles means that complete characterization requires specification of $O(10^{23})$ atomic coordinates. However, few are macroscopically relevant. These are the thermodynamic coordinates.

- Only few combination of atomic coordinates that are time-independent are macroscopically observable.

- *Classical* Thermodynamics describes only static states of macroscopic systems. Example: Volume, Pressure, Temperature

- *C.TD* studies the interaction between material systems and environment through energy flows. It also studies how the properties of the system are affected through those interactions.

Thermodynamic Systems

- A thermodynamic system is any physical system, whose properties can be defined.

- A description of a thermodynamic system requires specifications of walls that separate it from its surrounding. These walls specify the way the system interacts with the environment. They act as boundary conditions:

    - Rigid/Deformable→"flow of volume"→ Mechanical Work.
    - Adiabatic/Diathermal→"flow of entropy"→ Heat.
    - Non-permeable/Permeable→"flow of matter"→ Chemical Work.

Variables

- Extensive: Scale w/size of system (U,S,N,V)

- Intensive: Do not scale w/size of system (T,P,μ)

- State Variable: Quantities Needed to Describe *Equilibrium* State of the System

- Important: Only at equilibrium, or very near to equilibrium, are the thermodynamic properties clearly defined.

First Law

- Internal Energy: Any way of storing energy: Mechanical, Electrical, Chemical, Thermal

- Energy Flows:

– Work: Energy transfer resulting from displacement under a force: Mechanical, Electrical, Magnetic, Surface, Chemical

- Energy in any isolated system is conserved. The universe is a perfectly isolated system, and therefore $\triangle U_{Universe} = 0$. Alternatively: In any process, energy is conserved:

$$dU = \delta W + \delta Q$$

Note that W is any kind of work. For simplicity, we can consider that $\delta W = -PdV + \mu dN$.

- U is a state function. Its value depends on the current value of some other thermodynamic parameters. The difference in value for a state function between two defined thermodynamics states is path-independent.

- Are both trajectories state functions?

$$ds=(dx^2+dy^2)^{1/2}$$
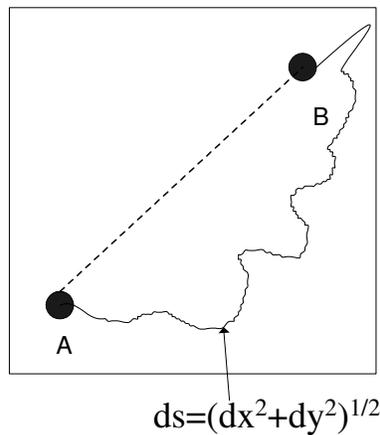
Figure 1: Are both trajectories state functions??

- Work and Heat are not state functions. They depend on the actual process that takes the system from state A to state B.

- A function $A(x, y)$ has a perfect differential (dA) if:

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy$$

and

$$\frac{\partial^2 A}{\partial x \partial y} = \frac{\partial^2 A}{\partial y \partial x}$$

- Enthalpy: $H \equiv U + PV$

Change in Internal Energy of an Ideal Gas

For an ideal gas, the change in internal energy is only a function of temperature. In class, we used a constant volume process to show that:

$$dU = nC_V dT$$

Let's do the same for a constant pressure process:

$$dU = \delta Q)_P - P\, dV)_P$$

By definition,

$$\delta Q)_P \equiv nC_P dT$$

From the ideal gas equation of state $PV = nRT$ we have:

$$-P\, dV)_P = -P\frac{nR\, dT)_P}{P}$$

And dU is then given by:

$$dU = n\left(C_P - R\right) dT$$

For an ideal gas, it can be proven that $C_P - C_V = R$. Therefore:

$$dU = nC_V dT$$

Thus, for an **ideal gas**, a change in internal energy is **only** related to a change in temperature. An ideal gas can undergo any process you can think of, but its change in internal energy will always be just a function of the initial and final temperatures of the gas.

This does not hold for other mathematical descriptions of **real** gases, such as Van der Waals, etc...where the internal energy is not only a function of temperature, but of other intensive variables, such as pressure.

Heat Capacity

$$C \equiv \frac{Q}{T} = \frac{dQ}{dT}$$
$$c = \frac{1}{N}\frac{dQ}{dT}$$

(Normalized per Mol)

$$c_P = \frac{1}{N}\left.\frac{dQ}{dT}\right)_P$$
$$c_V = \frac{1}{N}\left.\frac{dQ}{dT}\right)_V$$
$$c_p > c_V$$

Enthalpy

$$H \equiv U + PV$$

Processes at constant P. The heat exchanged between a system and its surroundings during a process at constant pressure results in a change in the enthalpy of the system:

$$dH = \delta Q)_P + V dP$$
$$dH = \delta Q)_P$$

Note that this is true *only* when the only work term is PV work. If there is any other kind of work, such as electrical, etc., the relationships above do not hold.

Problem 1 A container with rigid walls and covered with asbestos is divided into two parts by a partition. One part contains a gas and the other is evacuated. If the partition is suddenly broken, show that the initial and final internal energies of the gas are equal.
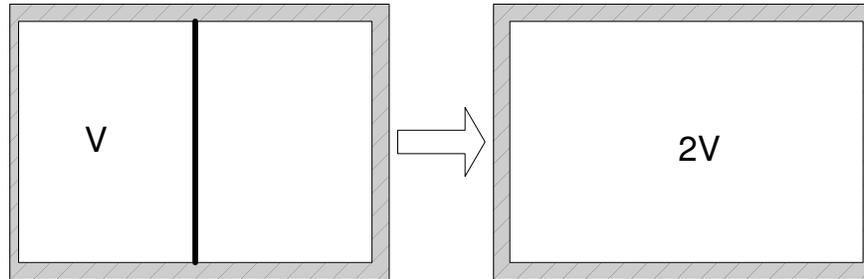
Figure 2: Free Expansion

Problem 2 One m^{3}of diatomic ideal gas is expanded from an initial state at 298K and 15atm pressure to a final state at 2 atm and 298K.

a) What is the volume of the gas after the expansion ?

b) What is the amount of work done by the gas if the temperature remained constant during the expansion.

c) What is the amount of work done if the gas is thermally insulated from its environment during the expansion to 2atm and then allowed to cool (or warm) back to 298K, keeping the pressure constant at 2atm. ? It might be helpful if you draw the processes on an appropriate state diagram.