Thermodynamics: The Zeroth and First Laws

PHYS 301; Prof. Cyr-Racine

1 Introduction to Thermodynamics

So far in this course, we have focused on statistical mechanics, studying systems in terms of their microscopic constituents. By contrast, thermodynamics doesn't care about atoms and microscopic degrees of freedom. It instead describes relationships between observable macroscopic phenomena.

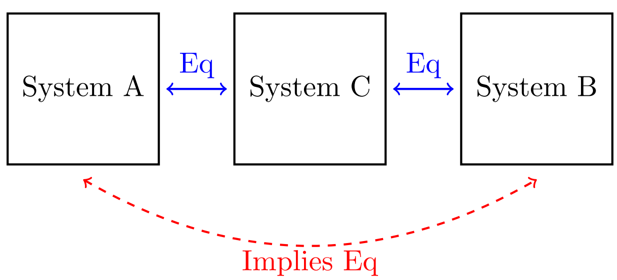
Key advantage: By abstracting out the microphysics of systems, it leads to very general and broadly applicable conclusions that are independent of any specific system.

Since thermodynamics predates statistical mechanics, we need to reset our notion of temperature, energy, and entropy.

2 The Zeroth Law and Temperature

Equilibrium: An isolated system, when left alone for a suitably long time, will relax to a state where no further change is noticeable. This is state is said to be in equilibrium.

Zeroth Law: If two systems, A and B, are each in thermal equilibrium with a third system C, then they are also in thermal equilibrium with each other.



This empirical observation implies the existence of a function of state such that if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$. This function is, of course, the **temperature**.

Thus, the Zeroth Law establishes the existence of a function called temperature. It doesn't tell us *what* the temperature is, just that it exists. For a gas at pressure P and in volume V, we must have an equation of state:

$$T = T(P, V) \tag{1}$$

For example, for an ideal gas, $T = \frac{PV}{Nk_B}$.

3 The First Law of Thermodynamics

First Law: The amount of work required to change an adiabatically isolated system from state 1 to state 2 is independent of how the work is performed.

This implies the existence of a state function, the **internal energy** E. For an adiabatic process, the work done on the system is exactly the change in internal energy: $W_{\text{adiabatic}} = \Delta E$.

If the system is *not* adiabatically isolated, the work done W is generally not equal to ΔE. The difference is defined as the **heat** Q added to the system:

$$\Delta E = Q + W \tag{2}$$

Because E is a state function, ΔE only depends on the initial and final states. However, Q and W depend strongly on the path taken between those states. Consequently, there are no functions of state $Q(P, V)$ or $W(P, V)$ for a gas.

4 Quasi-Static Processes and Infinitesimal Form

In our discussion above, the First Law is valid no matter how quick or violent the energy transfer to the system is. However, to compute things explicitly, we will only consider processes that add or subtract energy very slowly, such that the system is always in equilibrium. Such processes are called **quasi-static**.

Consider the First Law in infinitesimal form. Since $E(P, V)$ is a state function, its infinitesimal change is an exact differential (a total derivative):

$$dE = \frac{\partial E}{\partial P} dP + \frac{\partial E}{\partial V} dV \tag{3}$$

However, for heat and work, dQ and dW are not actual derivatives; they represent small amounts of heat and work. To emphasize this, we introduce a new notation using $đ$ to denote inexact differentials: $đQ$ and $đW$.

In the language of differential forms, dE, $đW$, and $đQ$ are all one-forms; dE is exact, while $đQ$ and $đW$ are not. The First Law in infinitesimal form is written as:

$$\boxed{dE = đQ + đW} \tag{4}$$

4.1 Work in Gas Systems

We will mostly focus here on gas systems, for which the infinitesimal work done *on* the gas is:

$$đW = -P dV \tag{5}$$

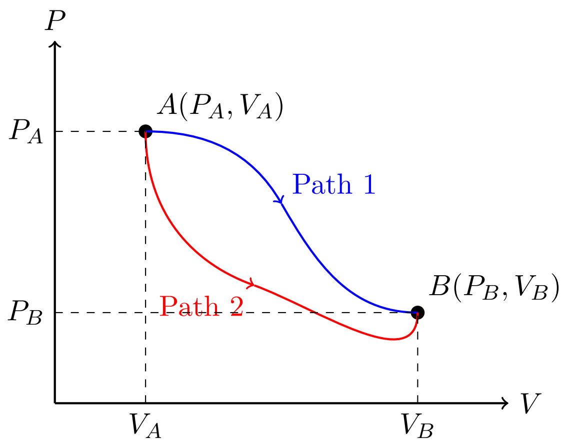
Meaning of $đW = -PdV$:

- If $dV < 0$ (compression), then $đW > 0$ (work is done *on* the gas).
- If $dV > 0$ (expansion), then $đW < 0$ (work is done *by* the gas).

Because $đW$ is an inexact differential, there is no state function $W(P, V)$ such that integration yields a path-independent result.

5 Path Dependence

Consider a gas system going from an initial state $A(P_A, V_A)$ to a final state $B(P_B, V_B)$ quasi-statically along two different paths:



By the First Law, the change in internal energy is path-independent:

$$\Delta E = \int_{\text{Path 1}} dE = \int_{\text{Path 2}} dE = E_B - E_A \tag{6}$$

However, the total work done is the negative area under the $P-V$ curve: $W = -\int PdV$. Since the area under Path 1 is clearly larger than the area under Path 2, the work done is path-dependent ($W_1 \neq W_2$).

Consequently, to ensure that ΔE remains the same for both paths, the heat added to the system must also be path-dependent ($Q_1 \neq Q_2$).