Given a system where the volume (V) and number of particles (N) do not change, how do we calculate a change in entropy (S) or energy (U)?
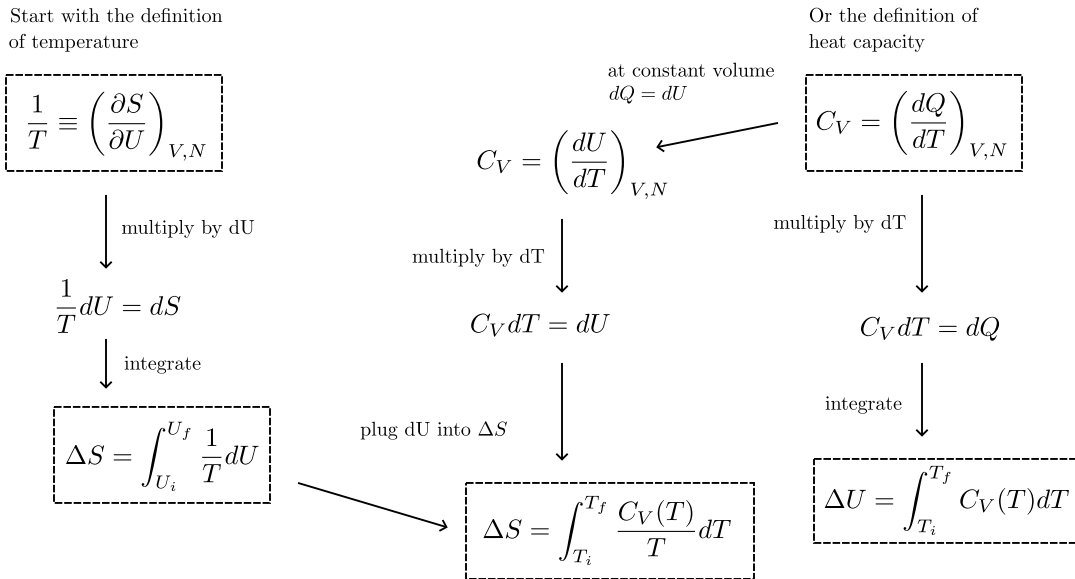
Start with the definition of temperature

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

multiply by dU

$$\frac{1}{T}dU = dS$$

integrate

$$\Delta S = \int_{U_i}^{U_f} \frac{1}{T}dU$$

at constant volume $dQ = dU$

$$C_V = \left(\frac{dU}{dT}\right)_{V,N}$$

Or the definition of heat capacity

$$C_V = \left(\frac{dQ}{dT}\right)_{V,N}$$

multiply by dT

$$C_V dT = dU$$

multiply by dT

$$C_V dT = dQ$$

plug dU into ΔS

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T}dT$$

integrate

$$\Delta U = \int_{T_i}^{T_f} C_V(T)dT$$

Figure 1: Entropy, energy, heat capacity, and temperature are all connected to one another through derivatives and integrals.

4 Entropy of physical systems

- Be able to compute the entropy change as two bricks come into equilibrium.

- Definition of temperature in terms of entropy: $\frac{1}{T} = \frac{dS}{dU}$

- Pressure in terms of entropy: $\frac{p}{T} = \frac{dS}{dV}$

- Fundamental relation: $dS = \frac{dQ}{T}$

- Heat capacity and entropy: $\Delta S = \int \frac{C}{T}dT$

4.1 The "two bricks" model

For this section, we will consider a very simple model of two bricks that are in internal equilibrium, but different temperatures. It doesn't matter that they are bricks! They could be any objects. We will explore how maximizing entropy leads us to a thermodynamic definition of temperature, and compute how much entropy increases as the two bricks come into equilibrium with each other.

4.2 Definition of temperature

The total entropy of the two-brick system is

$$S_{tot} = S_1(U_1) + S_2(U_2). \tag{1}$$

We are assuming that the volume and number of particles in the bricks stays the same, so we are only going to consider the dependence on internal energy. As we determined in the previous section, spontaneous processes stop happening when the entropy is maximized. Also due to conservation of energy, we know that $U_1 + U_2 = C$, where C is some constant.

To maximize entropy, we take the derivative and set it equal to zero:

$$\frac{dS_1}{dU_1} + \frac{dS_2}{dU_1} = 0. \tag{2}$$

Note that we had to take the derivative of the entropy of both bricks with respect to U_1. However, we have the function $S(U_2)$. Using conservation of energy, we can find that $\frac{dU_1}{dU_2} = -1$. Using the chain rule, we have

$$\frac{dS_2}{dU_1} = \frac{dS_2}{dU_2}\frac{dU_2}{dU_1} = -\frac{dS_2}{dU_2}. \tag{3}$$

This makes some sense in retrospect; an increase in U_1 is a decrease in U_2, so the derivatives should be opposite sign.

So finally we can find the **equilibrium relation**:

$$\frac{dS_1}{dU_1} = \frac{dS_2}{dU_2}. \tag{4}$$

Note that entropy has units of J/K and internal energy has units of J, so the derivative has units of 1/K. This is very suggestive, and indeed it turns out that if you define

$$\frac{dS_1}{dU_1} \equiv \frac{1}{T_1}, \tag{5}$$

then we get the same behavior as we noted empirically in this class–energy spontaneously flows from high temperature to low temperature until the two bricks are the same temperature.

The reason that maximization of entropy is such an important concept is that it allows us to derive many other **equilibrium conditions** like $T_1 = T_2$.

4.3 Fundamental relation for constant volume

Now we'll derive a very useful relationship for the change in entropy during a process. If during the process, everything is held constant other than the internal energy U, then using the chain rule:

$$\frac{dS}{dt} = \frac{dS}{dU}\frac{dU}{dt} = \frac{1}{T}\frac{dU}{dt}. \tag{6}$$

Here we used a time derivative to give a sense of a process, but often in thermodynamics we are lazy and instead write the same equation as

$$dS = \frac{1}{T}dU \tag{7}$$

4.4 Definition of pressure in terms of entropy

We can define pressure similarly to temperature. Consider a chamber with a movable membrane as noted in Fig 4.4. We can do the same trick as with energy to get
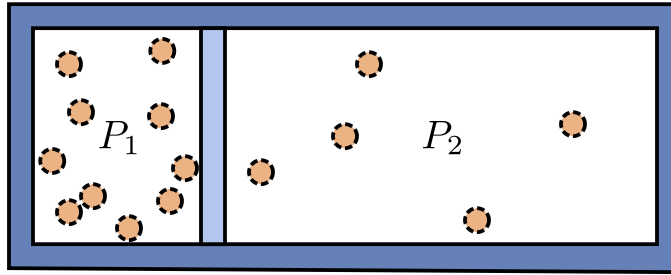
$$\frac{dS_1}{dV_1} = \frac{dS_2}{dV_2}. \tag{8}$$

The units of $\frac{dS}{dV}$ are J/K m^3, which doesn't look like much of anything, but recall that J = N m, which means the units are also N/m^2 K. Pressure has units of force per area, and temperature has units of Kelvin. So one might guess that

$$\frac{dS}{dV} \equiv \frac{p}{T} \tag{9}$$

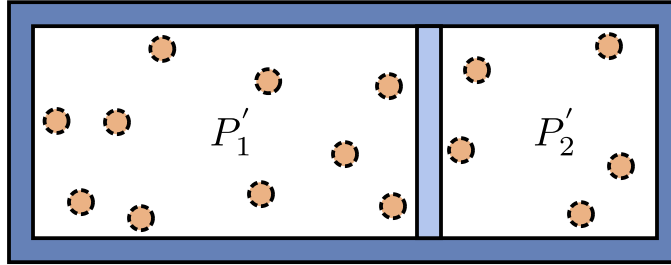in analogy to temperature and energy.

Figure 2: Consider a chamber with a free-moving partition between its two sides. The volume of each side changes as the partition slides back and forth. This system is in equilibrium when the wall between the two sides stops moving, or (equivalently) when the pressure on one side is equal to the pressure on the other. This condition maximizes the total entropy.

4.5 Fundamental relation for changing volume and energy

Now we can compute the change in entropy for any quasistatic process (even if both pressure and volume are changing) by using the equivalent of the chain rule for multiple dimensions:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \frac{1}{T}dQ, \tag{10}$$

where we used the first law to substitute $dQ = dU + pdV$. This is the most general version of the fundamental relation, so long as the number of particles in the system is not changing. This was actually the original definition of entropy when thermodynamics was being developed. In the modern understanding, this relation is a result of the second law of thermodynamics, the definitions of temperature and pressure in terms of entropy, and some calculus.

4.6 Relationship between heat capacity and entropy

As we've mentioned before, it is often very difficult to measure the total entropy and total internal energy of an object. It actually is very easy to measure the heat capacity; simply transfer a known amount of heat Q into the object, and measure how much the temperature changes. Then $C = \frac{dQ}{dT} \simeq \frac{Q}{\Delta T}$, if the change in temperature is small enough. We can then compute the entropy change as follows:

$$\Delta S = \int dS = \int \frac{1}{T}dQ. \tag{11}$$

Remember that the temperature T changes as we put heat into the material, though, so we cannot just pull the temperature out of the integral. We have to either change our integration variable so we are integrating over T, or write T as a function of Q. The easier path is to change the integration variable from Q to T.

We do that using the definition of heat capacity: $C = \frac{dQ}{dT}$, so $dQ = CdT$. Then

$$\Delta S = \int_{T_i}^{T_f} \frac{C}{T} dT. \tag{12}$$

Keep in mind that sometimes the heat capacity can depend on temperature! If it does then you will need to include that dependence when integrating.