4

Entropy (I) - thermodynamic perspective

Entropy is an essential concept arising from thermodynamics. Later on its microscopic nature was revealed as a description of disorderness. Its importance spread to many aspects of modern sciences including information science and life science.

In the last lecture, we have defined the reversible and irreversible thermodynamic processes and the Carnot cycle. Carnot proved that the efficiency of an irreversible thermal engine does not depend on the concrete designs and working substances. It only depends on the nature of the high and low temperature heat reservoirs, i.e., temperatures. The internal energy of a system $U(P, V, N)$ is a function of state, *i.e,* if the particle number N, volume V, pressure P, are given, then U is determined. If the system completes a cycle and returns its original state, its internal energy does not change, i.e.,

$$\oint dU = 0. \tag{4.1}$$

In other words, dU is a total derivative, which is similar to the potential function we learned in mechanics. Indeed, U is called a thermodynamic potential.

In contrast the heat transfer Q is a process-dependent quantity. Typically speaking, for a closed cycle, $\oint dQ = -\oint dW \neq 0$. Naturally, it would be interesting to explore whether it is possible to design a heat-related quantity as a state function, and then its change is a total derivative.

4.1 Clausius' theorem

In order to define a heat related total derivative, Clausius proved the following theorem.

Clausius' theorem: For any cyclic process for a closed system which interacts with the environment via heat transfer and work, it satisfies

$$\oint \frac{dQ}{T} \leqslant 0, \tag{4.2}$$

in which the equality holds when the entire process is reversible.
Proof: Denote the cyclic process O. During different steps of the process, the system contacts different heat reservoirs, say, R_1 with temperature T_1, R_2 with temperature T_2, ..., respectively. At each step, the system transfers heat ΔQ_i whose signs ± mean heat absorption and release, respectively.

ΔQ_i's are transferred at different temperatures T_i, hence, they cannot be compared at an equal basis. They should be properly normalized for comparison. For this purpose, let us introduce a standard heat reservoir R_0 whose temperature is defined as the temperature standard T_0.

Next, we bring a Carnot thermal engine working between the R_0 and each heat reservoir R_i. The Carnot engine is run in the cycle in the following way: Since Q_i is taken out of the reservoir R_i during the cycle O, let the Carnot engine input Q_i back to R_i, such that each reservoir has zero net heat transfer. Meanwhile Q_i^0 is transferred from the standard reservoir to the Carnot engine, then

$$\frac{Q_i^0}{Q_1} = \frac{T_0}{T_1}. \tag{4.3}$$

The total amount of heat extracted from the standard reservoir is

$$Q_{tot} = \sum_i Q_i^0 = T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i}. \tag{4.4}$$

Hence, after running the cycle O followed by the series of Carnot cycles between R_i and R_0, the net effect is to extract Q_{tot} from the standard reservoir R_0 and convert it to work. This is impossible if $Q_{tot} > 0$, which would violate the 2nd law of thermodynamics. It is ok if $Q_{tot} < 0$ such that work can be completely converted into heat. Hence,

$$\sum_{i=1}^{N} \frac{Q_i}{T_i} \leqslant 0. \tag{4.5}$$

Its continuous form becomes

$$\oint \frac{dQ}{T} \leqslant 0. \tag{4.6}$$

If the cycle O is reversible, we can reverse all the steps above, then

$$\oint -\frac{dQ}{T} \leqslant 0. \tag{4.7}$$

Combine Eq. 4.6 and Eq. 4.7, the following conclusion is arrived

$$\oint \frac{dQ}{T} = 0, \tag{4.8}$$

i.e., dQ/T is a total derivative for reversible processes.

4.2 Entropy as a state function

Based on Eq. 4.8, we are able to construct a new thermodynamic potential – entropy S for a thermodynamic system, which was defined by Clausius in 1850s. Considering two states "a" and "b", we design a reversible process following a path to connect them, then

$$S(b) - S(a) = \int_a^b dS = \int_a^b \frac{dQ}{T}. \tag{4.9}$$

As long as the process is reversible, $S(b) - S(a)$ is path independent.

We can write down the differential form for the 1st law of thermodynamics for a reversible process as

$$dU = dW + \delta Q = -pdV + TdS. \tag{4.10}$$

If the process connecting states a and b is irreversible, Eq. (4.9) is no longer held. Suppose we complete such an irreversible process from a to b, and then move back from b to a following a reversible process. Overall such a cycle is irreversible, hence,

$$0 > \oint \frac{dQ}{T} = \int_{a,irr}^b \frac{dQ}{T} + \int_{b,rev}^a \frac{dQ}{T} = \int_{a,irr}^b \frac{dQ}{T} + S(a) - S(b), \tag{4.11}$$

then

$$S(b) - S(a) > \int_{a,irr}^b \frac{dQ}{T}. \tag{4.12}$$

Now we have an important result: An isolated system has the tendency to increase its entropy. For a thermally isolated system evolving from state a to b, if the process is irreversible then

$$S_b - S_a > \int_{a,irr}^b \frac{dQ}{T} = 0, \tag{4.13}$$

which means that an isolated system has the tendency to increase entropy.

4.3 Negative temperature

Consider two systems 1 and 2 at temperatures T_1 and T_2, respectively. Then we bring them to contact together, and after some time, they reach thermal equilibrium. The total entropy change with time t should increase

$$\frac{ds}{dt} = \frac{ds_1}{dt} + \frac{ds_2}{dt} = \left(\frac{\partial s_1}{\partial E_1}\right)_T \frac{dE_1}{dt} + \left(\frac{\partial s_2}{\partial E_2}\right)_T \frac{dE_2}{dt} > 0. \tag{4.14}$$

Since $\frac{dE_1}{dt} + \frac{dE_2}{dt} = 0$, we arrive at

$$\frac{ds}{dt} = \frac{dE_1}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0. \tag{4.15}$$

Assume heat flows from system 1 to 2, i.e., $\frac{dE_1}{dt} < 0$, then $\frac{1}{T_1} < \frac{1}{T_2}$, i.e., $T_1 > T_2$. Hence, heat transfer is from a high temperature system to a low temperature system.

Actually, there is another possibility. Although the thermodynamic temperature is defined as positive, if we extrapolate its definition to negative value, it is fine to have $T_1 < 0$, and $T_2 > 0$. The heat flows from a negative temperature to a positive temperature, hence, a negative temperature is actually higher than a positive temperature.

Then what do we mean temperature can be negative? Since $1/T = \partial S/\partial E$, a negative temperature means that as energy E increases the entropy S drops. Later on, we will see that the number of microscopic states scales as e^{s/k_B}, hence, as E increases the states of matter decreases, which is highly unusual. Nevertheless, we will provide an example in the HW.

If both $T_1 < 0$ and $T_2 < 0$, by keeping $\frac{dE_1}{dT} < 0$, we would arrive

$$\frac{1}{|T_1|} > \frac{1}{|T_2|}, \tag{4.16}$$

which means $|T_1| < |T_2|$. Hence, 0^- the hottest temperature.

4.4 Why do we need to eat?

This is an interesting and deep question. An apparent answer is that our daily life activities consume energy and food is the supply. This is certainly correct, nevertheless, it does not touch the essence. For example, we cannot survive by just drinking hot water even though it also contains energy.

In order to be alive, a human needs to maintain his/her body temperature constant at $T \approx 310K$. We assume that he/she is the same at the beginning of each day, such that one-day life can be viewed as a cycle. Of course this is only an idealization, and no one can be immortal! Nevertheless, it is a good approximation within a short period of time. For this one-day life cycle, the entropy does not change since it is a function of state. The Clausius' theorem yields

$$0 = \oint ds > \frac{Q}{T}. \tag{4.17}$$

$Q < 0$ means that heat is released from the body into the environment. Since $\Delta U = W + Q = 0$,

$$W = -Q > 0. \tag{4.18}$$

This is not the mechanical work, but the one in the general sense, i.e. the energy without entropy. It is the energy stored in chemical bonds, such as in glucose. Chemical bonds are like elastic springs with tension, and the bonding energy is typically at the order of 1eV. When a chemical bond is broken, energy is release to do work.

To be more precise, let us look inside the life cycle. Our body has a natural tendency of entropy increase. Wastes are produced during the irreversible life process – just like that a room becomes messy as time evolves if no one cleans it. Hence, we divide the daily entropy change in our body into two parts: 1) The increase from the irreversibility, $\Delta S_1 > 0$, and 2) the decrease from the heat release $0 > \Delta S_2 > Q/T$. Since the total entropy change should be zero, i.e., $|\Delta S_1| = |\Delta S_2|$,

$$W = |Q| > T|\Delta S_2| = T|\Delta S_1|. \tag{4.19}$$

Even we lay flat all day without doing any work, eating is still necessary to remove the entropy ΔS_1 from the life irreversibility. In fact, the daily basal metabolism rate per unit body weight is roughly 25kcal/kg, hence, the daily entropy production rate R is roughly

$$\begin{aligned} R &= \frac{2.5 \times 10^4 \times 4.2}{310} \mathrm{J/(K.kg.day)} = 340 \mathrm{J/(K.kg)} \\ &= 2.4 \times 10^{25} k_B/(\mathrm{kg.day}) \end{aligned} \tag{4.20}$$

This amount of entropy needs to be removed through heat release. If only energy conservation matters, hot water is also fine as an energy supply. Nevertheless, its energy is of low quality which contains entropy. In comparison, food provides high quality energy with little entropy.