

Lecture 1 $\Rightarrow$ Nonequilibrium Thermodynamics. ①

Most of systems in nature (e.g. chemical reactions, biological systems, population dynamics) are out of equilibrium, whereas some of them (systems in contact with a single thermal reservoir) are "in equilibrium". This course will be devoted to the description of such systems, describing which quantities distinguish them.

In other cases, they present phase transitions among distinct steady state regimes.

General concepts

Thermal equilibrium is determined by the principle of maximal entropy. Take for instance an isolated system composed of two parts A and B: let x_K^A and x_K^B a given extensive variable (energy, volume, number of moles) of subsystems A and B, respectively. Taking into account that A+B is isolated, we have for any x_K s $\Rightarrow x_K^A + x_K^B = c_K$ and hence

$$dx_K^A = -dx_K^B \quad \left[\begin{array}{l} \text{above relation / condition} \\ \text{is equivalent to the} \\ \text{first law of Thermodynamics} \end{array} \right]$$

Since the total entropy S is given by

$$S = S_A + S_B \quad (\text{the entropy is an extensive quantity})$$

its derivative with respect to x_K^A (or x_K^B) reads:

$$\begin{aligned} \frac{\partial S}{\partial x_K^A} &= \frac{\partial S_A}{\partial x_K^A} + \frac{\partial S_B}{\partial x_K^A} \quad \text{or even} \\ &= \frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \end{aligned}$$

Hence

$$dS = \sum_K \left(\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \right) dx_K^A$$

In the thermal equilibrium $dS = 0$ (the total entropy is a maximum) and it follows that

$$\frac{\partial S_A}{\partial x_K^A} = \frac{\partial S_B}{\partial x_K^B}$$

$$\left(\begin{array}{l} \text{e.g. if } x_K^A = U_A \text{ and } x_K^B = U_B \Rightarrow \frac{1}{T_A} = \frac{1}{T_B} \\ x_K^A = V_A \text{ and } x_K^B = V_B \Rightarrow \frac{P_A}{T_A} = \frac{P_B}{T_B} \\ x_K^A = N_A \text{ and } x_K^B = N_B \Rightarrow \frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \end{array} \right)$$

and hence the maximization of total entropy at the equilibrium is equivalent to the equality of temperatures / pressures or chemical potentials.

On the other hand, in certain cases

$$\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \neq 0, \quad \text{even at the}$$

steady state regime. In such a case, it

follows that $ds = \sum_K \left(\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \right) dx_K^A > 0$, ⁽²⁾

according to the second law of thermodynamics.

By taking the derivative of above expression respect to the time, we have that

$$\sigma \equiv \frac{ds}{dt} = \underbrace{\sum_K \left(\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \right)}_I \underbrace{\frac{dx_K^A}{dt}}_{II} > 0.$$

The left side $\sigma \equiv \frac{ds}{dt}$ is called entropy production rate and it is always greater than zero.

$$\begin{aligned} \frac{ds}{dt} = 0 &\Rightarrow \text{equilibrium regime} \Rightarrow \left(\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \right) \frac{dx_K^A}{dt} = 0 \\ \frac{ds}{dt} > 0 &\begin{cases} \underbrace{\left(\frac{\partial S_A}{\partial x_K^A} - \frac{\partial S_B}{\partial x_K^B} \right)}_{F_K} > 0 \text{ and } \underbrace{\frac{dx_K^A}{dt}}_{J_K} > 0 \\ \underbrace{\left(\frac{\partial S_B}{\partial x_K^B} - \frac{\partial S_A}{\partial x_K^A} \right)}_{F_K} > 0 \text{ and } \underbrace{\frac{dx_K^A}{dt}}_{J_K} < 0 \end{cases} \end{aligned}$$

The quantity (I) is called "thermodynamic force", whereas (II) is its "current/flux". When $\frac{ds}{dt} > 0$, it is associated with the force.

$F_K > 0$, its flux $J_K > 0$ and $F_K < 0$, $J_K < 0$.

In other words, if $K = u$ the flux J_u is from the hot temperature (body) to the cold one and so on. When $K = N$, the particle flux J_N is from the larger chemical potential to the lower one.

The entropy production is a property of the composite system $A+B$ and discerns equilibrium systems ($\frac{ds}{dt} = 0$) from nonequilibrium systems ($\frac{ds}{dt} > 0$).

Above equation can also be rewritten under a more convenient way

$$\sigma \equiv \frac{ds}{dt} = \sum_K \underbrace{F_K J_K}_{\text{sum of "forces times fluxes"}} \geq 0$$

Hence, in contrast to the energy, particle number and volume, the entropy production is not conserved, but always increases.

There is a difference between steady state regime and equilibrium/nonequilibrium regime. The former case refers to the time evolution of the system. After a some time, it will evolve to a "steady" regime in which certain quantities are constant. This happens in both equilibrium and nonequilibrium systems.

On the other hand, equilibrium systems does not have entropy production rate ($\sigma = 0$) in the steady state regime, whereas nonequilibrium system does ($\sigma > 0$).

Another feature distinguishing equilibrium and nonequilibrium systems is the so-called detailed balance condition, which can be described as follows.

An important regime is when $B \gg A$, e.g. the subsystem B will act as a thermal/particle reservoir.

In such case $f_k^B = \frac{\partial S_B}{\partial x_k^B} \approx cte$ and B will always close to the equilibrium and will act as a reservoir of A . One can assume, in this limit, that the entropy production is only due to the subsystem A since the dynamics of B is about reversible.

From the expression

$$\sigma^{(1)} = \sum_k \left(\frac{\partial S_A}{\partial x_k^A} - \frac{\partial S_B}{\partial x_k^B} \right) J_k$$

one can be rewritten as

$$\sigma^{(1)} = \frac{dS_A}{dt} + \phi(t), \text{ where}$$

$$\frac{dS_A}{dt} = \sigma(t) - \phi(t).$$

Since $f_k^B \equiv \frac{\partial S_B}{\partial x_k^B} \approx cte \Rightarrow \phi(t) = -\sum_k f_k^B J_k$ is called entropy flux and it is due only to the thermal bath according to whether $J_k < 0$ or $J_k > 0$, respectively.

Since the entropy S_A (the entropy of the subsystem A) will reach a time independent value in the steady state regime $\left(\frac{dS_A}{dt} = 0 \right)$,

it follows that

$$\sigma = \phi.$$

The regime will be equilibrium if

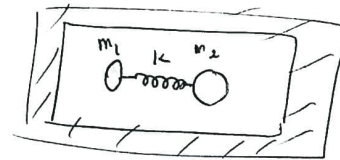
$$\sigma = \phi = 0,$$

whereas it will be a nonequilibrium regime (NESS)

$$\sigma_{NESS} = \phi_{NESS} \neq 0.$$

Below an example illustrating the difference between equilibrium and NESS.

(I)

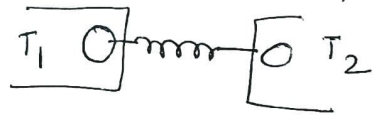


Two harmonic particles coupled with a spring of constant k in

contact with an unique Thermal reservoir of temperature T . Each particle is also subject to harmonic forces with spring constant k^* .

Even initially (at $t=0$) the system produces entropy ($\sigma(t) > 0$) it will evolve, after some time, to an equilibrium steady state and $\sigma(t \rightarrow \infty) = 0$.

④ Conversely, let us take the ^{same} system, but the left ^{and right} particles are coupled to thermal reservoirs of temperatures T_1 and T_2 , respectively. One can show that for long time ($t \rightarrow \infty$)

$$\sigma = \phi_{NESS} = \frac{\gamma L^2 (T_1 - T_2)^2}{2(L^2 + K\gamma^2) T_1 T_2}$$


where $L = \frac{K}{m}$, $K = \frac{(k + k^*)}{m}$ are spring

constants due to the coupling and individual harmonic forces, respectively. Note that when $T_1 = T_2$, one recovers the thermal equilibrium.

Next we are going to rediscover such concepts in terms of the framework of Stochastic Thermodynamics in which the time evolution of probability distribution is considered and related to the thermodynamic quantities.

Markovian systems and Master equation ⑤

The biggest difficulty of describing relaxation toward the steady state is that it depends on the details of the system and how it is coupled to the bath (reservoir). The master equation constitutes a marvelous and simpler approach to describe systems and one assumes the occurrence of a given event (stochastic process) solely depends on its value of the previous time instant.

Let P_n the probability of the system be in the microscopic state n ($n=0, 1, \dots, \infty$) where

$$\sum_{n=0}^{\infty} P_n = 1 \quad (\text{the probability distribution is normalized}),$$

its time evolution is ruled by the master equation

$$\frac{dP_n}{dt} = \sum_m W_{nm} P_m(t), \quad (1)$$

where W_{nm} denotes the transition rate (probability per unit of time from the state m to the state n).

The transition rate $W_{nm} \geq 0$ if $(n \neq m)$.

In particular, since the total probability is normalized $\frac{d}{dt} \sum_n P_n(t) = 0$ and hence

$$\sum_{n \neq m} W_{nm} P_m(t) = 0, \quad \text{which}$$

implies that

$$\sum_n W_{nm} = 0. \quad \left(\begin{array}{l} \text{The sum of transition} \\ \text{rates from } \underline{m} \text{ to} \\ \text{all } n\text{'s are zero} \end{array} \right)$$

above expression can also be rewritten more conveniently as

$$\sum_{n \neq m} W_{nm} + W_{mm} = 0 \Rightarrow W_{mm} = - \sum_{n \neq m} W_{nm}$$

By substituting in Eq. (1) we have that

$$\begin{aligned} \frac{dP_n}{dt} &= \sum_{m \neq n} W_{nm} P_m(t) + W_{nn} P_n(t) \\ &= \sum_{m \neq n} \left[W_{nm} P_m(t) - W_{mn} P_n(t) \right] \end{aligned}$$

The term $W_{nm} P_m(t)$ takes into account all possible transitions $m \rightarrow n$ that contributes for the "increasing" of $P_n(t)$ [gain term], whereas

the term " $W_{mn} P_n(t)$ " contributes for the decreasing of $P_n(t)$.

In the steady state, $\frac{d}{dt} P_n = 0$ and

one has that

$$\sum_{m \neq n} [W_{nm} P_m(t) - W_{mn} P_n(t)] = 0.$$

The system will reach an equilibrium steady state if the condition

$$W_{nm} P_m(t) - W_{mn} P_n(t) = 0 \quad \text{is}$$

satisfied for all pairs of states n and m. Such above condition is known as "detailed balance condition" and it ensures that the system will reach the Boltzmann-Gibbs distribution. In other words, when transition rates W_{nm} and W_{mn} are related through condition

$$W_{nm} P_m(t) - W_{mn} P_n(t) = 0, \quad \text{the probability distribution } P_m(t) \longrightarrow P_m^{eq} = \frac{e^{-\beta \epsilon_m}}{Z} \quad \text{for large times.}$$

Conversely, when $W_{nm} P_m(t) - W_{mn} P_n(t) \neq 0$, the system will reach to a nonequilibrium steady state (NESS). As it will be shown further, in the NESS there is production of entropy.

In the appendix, I will derive the expressions for the master equation from the Markovian starting point.

The starting point of a stochastic description for Thermodynamics relies in the definitions of entropy and production of entropy.

We assume that the entropy, defined as

$$S(t) = -k_B \sum_m P_m(t) \ln P_m(t) = -k_B \left\langle \ln P_m(t) \right\rangle$$

↑
ensemble
average

for equilibrium systems (see e.g. the next

lectures in which I will derive such expression) in the canonical ensemble

is extended for nonequilibrium systems.

The second point is the definition of entropy production. In particular, we consider the definition (proposal) by Schnakenberg (Rev. Mod. Phys. 48 571 (1976)) given by

$$\sigma(t) = \frac{k_B}{2} \sum_m \sum_n (W_{nm} P_m(t) - W_{mn} P_n(t)) \ln \frac{W_{nm} P_m(t)}{W_{mn} P_n(t)}$$

The reliability of above expression can be understood that it is a function of form $(x-y) \ln \frac{x}{y}$, which is always greater than zero (positive), as one expects for the entropy production when

$W_{nm} P_m(t) - W_{mn} P_n(t) \neq 0$ (nonequilibrium regime where the detailed balance is violated).

But, when $W_{nm} P_m(t) - W_{mn} P_n(t) = 0$,

$$\sigma(t) = 0 \quad (\text{as should it be}).$$

Thus, the definition by Schnakenberg is a "good" definition of entropy production.

One can relate $S(t)$ and $\sigma(t)$ by taking $\frac{dS(t)}{dt}$ and relating to the master equation.

$$\begin{aligned}\frac{dS}{dt} &= -K_B \frac{d}{dt} \sum_m P_m(t) \ln P_m(t) \\ &= -K_B \sum_m \frac{dP_m}{dt} \ln P_m(t) - K_B \sum_m P_m(t) \frac{1}{P_m(t)} \frac{dP_m}{dt}\end{aligned}$$

The second right term is zero since $\sum_m \frac{dP_m}{dt} = 0$, due to the normalization of probability.

Hence

$$\frac{dS}{dt} = -K_B \sum_m \sum_{n \neq m} \{W_{nm} P_m(t) - W_{mn} P_n(t)\} \ln P_m(t)$$

or even

$$= -K_B \sum_m \left(\sum_n W_{mn} P_n(t) \right) \ln P_m(t)$$

By summing the null term $+ K_B \sum_m \left(\sum_n W_{nm} \right) P_m \ln P_m$

we have that

$$\frac{dS}{dt} = -K_B \sum_m \sum_n \{W_{mn} P_n(t) - W_{nm} P_m(t)\} \ln P_m(t)$$

or even rewritten as

$$= -K_B \sum_m \sum_n W_{mn} P_n(t) \ln \frac{P_m(t)}{P_n(t)} = \frac{K_B}{2} \sum_{m,n} (W_{mn} P_n(t) - W_{nm} P_m(t)) \ln \frac{P_n}{P_m}$$

$$= \frac{K_B}{2} \sum_{m,n} (W_{mn} P_n(t) - W_{nm} P_m(t)) \ln \frac{P_n}{P_m}$$

Note that $\frac{dS}{dt} = \sigma(t) - \phi(t)$, where

$$\sigma(t) = \frac{K_B}{2} \sum_{m,n} (W_{mn} P_n(t) - W_{nm} P_m(t)) \ln \frac{W_{mn} P_n}{W_{nm} P_m}$$

and

$$\phi(t) = \frac{K_B}{2} \sum_{m,n} (W_{mn} P_n(t) - W_{nm} P_m(t)) \ln \frac{W_{nm}}{W_{mn}}$$

Thus, the formulation of master equation (Markovian systems with discrete sets of states) provides us a clear distinction between equilibrium and nonequilibrium steady states.

Summarizing our findings:

$$\text{Equilibrium} \Rightarrow W_{mn} P_n^{eq} - W_{nm} P_m^{eq} = 0.$$

$$P_n^{(eq)} = \frac{e^{-\beta \epsilon_n}}{Z}$$

$$\sigma = \phi = 0.$$

$$\text{Nonequilibrium} \Rightarrow W_{mn} P_n(t) - W_{nm} P_m(t) \neq 0$$

$$\sigma_{NESS} = \phi_{NESS} \neq 0. \quad (\text{steady state})$$

Above expressions can also be interpreted in terms of forces times fluxes.

$$\sigma = \sum_{m > n} J_{mn} X_{mn}, \text{ where}$$

$$J_{mn} = W_{mn} P_n(t) - W_{nm} P_m(t)$$

$$X_{mn} = k_B \ln \frac{W_{mn} P_n}{W_{nm} P_m}$$

When $X_{mn} = 0 \Rightarrow J_{mn} = 0$, in consistency

with the previous initial findings from page 2

The connexion with macroscopic variables (e.g. temperature) can be conveniently done by assuming that there is a parameter that changes into the time (e.g. energy levels changing into the time), in such a way that the system fulfills the "local detailed balance", but globally it does not obey. I will return to this point in the future.

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First law of Thermodynamics

Until here, we have talked about the second law of Thermodynamics, but we have not talked about anything about the conservation of energy.

Taking for instance the mean energy

$$u = \sum_m \epsilon_m^{(t)} P_m(t), \text{ where } \epsilon_m(t) \text{ and } P_m(t)$$

denote the m -th energy level value and its associated probability, respectively. As it will be discussed in the next lectures, in the case of equilibrium systems $P_m(t) = \frac{e^{-\beta \epsilon_m}}{Z}$.

By taking the time derivative of above expression, we have that

$$\frac{du}{dt} = \underbrace{\sum_m \dot{\epsilon}_m(t) P_m(t)}_{(I)} + \underbrace{\sum_m \epsilon_m(t) \dot{P}_m(t)}_{(II)}$$

The first term (I) is denoted "work" per time and it corresponds to the time variation of energy level by keeping $P_m(t)$ fixed.

We can understand this definition under distinct arguments:

First, $\dot{\epsilon}_m(t)$ can be performed from a given protocol $\lambda(t)$ (e.g. magnetic field / volume)

in such a way that
$$\dot{\epsilon}_m(t) = \underbrace{\frac{d\epsilon}{d\lambda}}_{\text{"resembles a response to the stimulus"}} \cdot \underbrace{\frac{d\lambda}{dt}}_{\text{variation of the protocol / stimulus}}$$

whereas $\frac{d\lambda}{dt}$

e.g. $\Rightarrow \lambda = H$

$$\frac{d\epsilon}{dH} \rightarrow m$$

$$\lambda = V$$

$$\frac{d\epsilon}{dV} \rightarrow p$$

Conversely, $\dot{\epsilon}_m$ the heat per time corresponds to the time variation of occupation / probability associated to the level m .

Note that $\frac{d\epsilon}{dt} - \dot{W} - \dot{Q} = 0$, in consistency with the first law of thermodynamics.

It is worth mentioning that while $\frac{d\epsilon}{dt}$ is a state function, the quantities $\dot{W}$ and $\dot{Q}$ are not.

Appendix: Markovian processes and Master equation dynamics. (11)

Let x_t a given ^(discrete) stochastic variable which takes integer values. Take for instance the time also discrete.

The stochastic process ^(fully) is characterized at the time $\underline{t}$ for the joint probability distribution

$$P_t(n_0, n_1, n_2, \dots, n_t).$$

It means that we are evaluating the probability at $\underline{t}$ in which x_t has the value n_0 at $t=0$,

n_1 at $t=1, \dots$ and so on.

The ^(stochastic) process is Markovian if

$$P_{t+1}(n_{t+1} / n_0, n_1, \dots, n_t) = P_{t+1}(n_{t+1} / n_t).$$

and hence the conditional probability in the left side (the variable x_t to take the value n_{t+1} ^{at $t+1$} solely depends on its value in the previous instant t).

Consequently the joint probability becomes

$$P_t(n_0, n_1, \dots, n_t) = P_t(n_t | n_{t-1}) P_{t-1}(n_{t-1} | n_{t-2}) \dots P_1(n_1 | n_0) P_0(n_0).$$

Consequently the probability $P_t(n_t)$ given by $P_t(n_t) = \sum_{n_0} \sum_{n_1} \dots \sum_{n_{t-1}} P_t(n_t, n_{t-1}, \dots, n_0)$ becomes

$$P_t(n_t) = P_t(n_t | n_{t-1}) P_{t-1}(n_{t-1})$$

The conditional probability $P_t(n_t | n_{t-1})$

can be interpreted as the transition probability from the "state" n_{t-1} to the "state" n_t and can be rewritten as

$$P_t(n) = \sum_m T(n, m) P_{t-1}(m), \quad (*)$$

where $T(n, m) \geq 0$ (probability) and

$$\sum_n T(n, m) = 1 \quad (\text{normalization}).$$

above expression (*) is valid for discrete time. We can use it for obtaining the master equation, in which a given stochastic process occurs at "continuous time".

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To do that, we suppose that transitions

~~occur~~ ~~are~~ between two microscopic states m and n occur at the time interval τ (assumed to be very small) and given by

$$T(n, m) = \tau W(n, m) \quad \text{if } n \neq m$$

$$\text{and } T(n, n) = 1 - \tau \Omega(n).$$

above expression can be understood by recalling / assuming that if τ is very small, the probability of remaining in the same state $m=n$ should be close to 1.

$$\text{Since } \sum_n T(n, m) = 1 \quad (\text{normalization}),$$

it follows that

$$\sum_{n \neq m} T(n, m) + T(n, n) = 1$$

Hence

$$\tau \sum_{n \neq m} W(m, n) + 1 - \tau \Omega(n) = 1$$

$$\tau \Omega(n) = \tau \sum_{m \neq n} W(m, n)$$

$$\Omega(n) = \sum_{m \neq n} W(m, n)$$

By substituting $T(n, m) = \tau W(n, m)$ and

$$T(n, n) = 1 - \tau \sum_{m \neq n} W(m, n) \quad \text{in the expression}$$

$$P_e(n) = \sum_m T(n, m) P_{e-1}(m) \quad \text{we have that}$$

$$P_e(n) = \tau \sum_{m \neq n} W(n, m) P_{e-1}(m) + P_{e-1}(n) - \tau \sum_{m \neq n} W(m, n) P_{e-1}(n)$$

Finally, we arrive at

$$\frac{P_e(n) - P_{e-1}(n)}{\tau} = \sum_{m \neq n} [W(n, m) P_{e-1}(m) - W(m, n) P_{e-1}(n)],$$

which we obtain the master equation by taking the limit $\tau \rightarrow 0$ and by ~~calling~~ naming $t = (e-1)\tau$

$$\frac{dP_n}{dt} = \sum_{m \neq n} [W(n, m) P_m(t) - W(m, n) P_n(t)]$$