# 3.1: Modeling the Approach to Equilibrium

## Equilibrium

A thermodynamic system typically consists of an enormously large number of constituent particles, a typical 'large number' being Avogadro's number, $N_A = 6.02 \times 10^{23}$ . Nevertheless, in *equilibrium*, such a system is characterized by a relatively small number of thermodynamic state variables. Thus, while a complete description of a (classical) system would require us to account for $\mathcal{O}\left(10^{23}\right)$ evolving degrees of freedom, with respect to the physical quantities in which we are interested, the details of the initial conditions are effectively forgotten over some microscopic time scale $\tau$, called the collision time, and over some microscopic distance scale, $\ell$, called the mean free path[1]. The equilibrium state is time-independent.

## The Master Equation

Relaxation to equilibrium is often modeled with something called the *master equation*. Let $P_i(t)$ be the probability that the system is in a quantum or classical state $i$ at time $t$. Then write

$$\frac{dP_i}{dt} = \sum_j \left( W_{ij}\, P_j - W_{ji}\, P_i \right) . \tag{3.1.1}$$

Here, $W_{ij}$ is the rate at which $j$ makes a transition to $i$. Note that we can write this equation as

$$\frac{dP_i}{dt} = -\sum_j \Gamma_{ij}\, P_j \, , \tag{3.1.2}$$

where

$$\Gamma_{ij} = \begin{cases} -W_{ij} & if\ i \neq j \\ \sum_k{}' W_{kj} & if\ i = j \, , \end{cases} \tag{3.1.3}$$

where the prime on the sum indicates that $k = j$ is to be excluded. The constraints on the $W_{ij}$ are that $W_{ij} \geq 0$ for all $i, j$, and we may take $W_{ii} \equiv 0$ (no sum on $i$). Fermi's Golden Rule of quantum mechanics says that

$$W_{ij} = \frac{2\pi}{\hbar} \left| \langle\, i \,|\, \hat{V} \,|\, j \,\rangle \right|^2 \rho(E_j) \, , \tag{3.1.4}$$

where $\hat{H}_0 \left|\, i \,\right\rangle = E_i \left|\, i \,\right\rangle$, $\hat{V}$ is an additional potential which leads to transitions, and $\rho(E_i)$ is the density of final states at energy $E_i$. The fact that $W_{ij} \geq 0$ means that if each $P_i(t=0) \geq 0$ , then $P_i(t) \geq 0$ for all $t \geq 0$ . To see this, suppose that at some time $t > 0$ one of the probabilities $P_i$ is crossing zero and about to become negative. But then Equation 3.1.1 says that $\dot{P}_i(t) = \sum_j W_{ij} P_j(t) \geq 0$ . So $P_i(t)$ can never become negative.

## Equilibrium distribution and detailed balance

If the transition rates $W_{ij}$ are themselves time-independent, then we may formally write

$$P_i(t) = \left( e^{-\Gamma t} \right)_{ij} P_j(0) \, . \tag{3.1.5}$$

Here we have used the Einstein 'summation convention' in which repeated indices are summed over (in this case, the $j$ index). Note that

$$\sum_i \Gamma_{ij} = 0 \, , \tag{3.1.6}$$

which says that the total probability $\sum_i P_i$ is conserved:

$$\frac{d}{dt} \sum_i P_i = -\sum_{i,j} \Gamma_{ij}\, P_j = -\sum_j \left( P_j \sum_i \Gamma_{ij} \right) = 0 \, . \tag{3.1.7}$$

We conclude that $\vec{\phi} = (1, 1, \ldots, 1)$ is a left eigenvector of $\Gamma$ with eigenvalue $\lambda = 0$. The corresponding right eigenvector, which we write as $P_i^{eq}$, satisfies $\Gamma_{ij} P_j^{eq} = 0$, and is a stationary ( time independent) solution to the master equation. Generally, there is

only one right/left eigenvector pair corresponding to $\lambda = 0$, in which case any initial probability distribution $P_i(0)$ converges to $P_i^{eq}$ as $t \to \infty$, as shown in Appendix I (§7).

In equilibrium, the net rate of transitions into a state $|\, i\,\rangle$ is equal to the rate of transitions out of $|\, i\,\rangle$. If, for each state $|\, j\rangle$ the transition rate from $|\, i\,\rangle$ to $|\, j\rangle$ is equal to the transition rate from $|\, j\rangle$ to $|\, i\,\rangle$, we say that the rates satisfy the condition of *detailed balance*. In other words,

$$W_{ij}\, P_j^{eq} = W_{ji}\, P_i^{eq}. \tag{3.1.8}$$

Assuming $W_{ij} \neq 0$ and $P_j^{eq} \neq 0$, we can divide to obtain

$$\frac{W_{ji}}{W_{ij}} = \frac{P_j^{eq}}{P_i^{eq}}\ . \tag{3.1.9}$$

Note that detailed balance is a stronger condition than that required for a stationary solution to the master equation.

If $\Gamma = \Gamma^t$ is symmetric, then the right eigenvectors and left eigenvectors are transposes of each other, hence $P^{eq} = 1/N$, where $N$ is the dimension of $\Gamma$. The system then satisfies the conditions of detailed balance. See Appendix II (§8) for an example of this formalism applied to a model of radioactive decay.

## Boltzmann's H-theorem

Suppose for the moment that $\Gamma$ is a symmetric matrix, $\Gamma_{ij} = \Gamma_{ji}$. Then construct the function

$$\mathsf{H}(t) = \sum_i P_i(t)\, \ln P_i(t)\ . \tag{3.1.10}$$

Then

$$\begin{aligned}\frac{d\mathsf{H}}{dt} &= \sum_i \frac{dP_i}{dt}\,\big(1 + \ln P_i\big) = \sum_i \frac{dP_i}{dt}\,\ln P_i \\ &= -\sum_{i,j} \Gamma_{ij}\, P_j \ln P_i \\ &= \sum_{i,j} \Gamma_{ij}\, P_j \big(\ln P_j - \ln P_i\big)\ ,\end{aligned}$$

where we have used $\sum_i \Gamma_{ij} = 0$. Now switch $i \leftrightarrow j$ in the above sum and add the terms to get

$$\frac{d\mathsf{H}}{dt} = \frac{1}{2}\sum_{i,j} \Gamma_{ij}\big(P_i - P_j\big)\,\big(\ln P_i - \ln P_j\big)\ . \tag{3.1.11}$$

Note that the $i = j$ term does not contribute to the sum. For $i \neq j$ we have $\Gamma_{ij} = -W_{ij} \leq 0$, and using the result

$$(x - y)\,(\ln x - \ln y) \geq 0\ , \tag{3.1.12}$$

we conclude

$$\frac{d\mathsf{H}}{dt} \leq 0\ . \tag{3.1.13}$$

In equilibrium, $P_i^{eq}$ is a constant, independent of $i$. We write

$$P_i^{eq} = \frac{1}{\Omega} \quad , \quad \Omega = \sum_i 1 \quad \Longrightarrow \quad \mathsf{H} = -\ln\Omega\ . \tag{3.1.14}$$

If $\Gamma_{ij} \neq \Gamma_{ji}$, we can still prove a version of the H-theorem. Define a new symmetric matrix

$$\overline{W}_{ij} \equiv W_{ij}\, P_j^{eq} = W_{ji}\, P_i^{eq} = \overline{W}_{ji}\ , \tag{3.1.15}$$

and the generalized H-function,

$$\mathsf{H}(t) \equiv \sum_i P_i(t)\, \ln\!\left(\frac{P_i(t)}{P_i^{eq}}\right) . \tag{3.1.16}$$

Then

$$\frac{d\mathsf{H}}{dt} = -\frac{1}{2}\, \sum_{i,j} \overline{W}_{ij} \left(\frac{P_i}{P_i^{eq}} - \frac{P_j}{P_j^{eq}}\right) \left[\ln\!\left(\frac{P_i}{P_i^{eq}}\right) - \ln\!\left(\frac{P_j}{P_j^{eq}}\right)\right] \leq 0 . \tag{3.1.17}$$

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