

Master equations

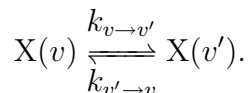
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1 State-to-state transitions and the master equation

In transition state theory, we assumed an equilibrium between the transition state and reactants. Another way to express this approximation is that we are assuming that the Boltzmann distribution governs the relative populations of all the states right up to the transition state. In RRK theory, we assumed rapid equilibration among the vibrational modes of a molecule. In both cases, it's not entirely whether our approximations are physically reasonable. When we want to study such questions, we have to think about the kinetics of transitions between quantum states of a molecule, which we call state-to-state transitions. These transitions can occur spontaneously (as is assumed to occur for the vibrational states in RRK theory), or they can be caused by collisions. We can study these questions in a very detailed way in quantum dynamics simulations, or in various kinds of experiments involving crossed molecular beams. These options provide very complete information on the state-to-state transitions, but are correspondingly resource-intensive. A middle ground is provided by the **master equation**, a set of rate equations for the probability that each state is occupied in any given molecule.¹ We can incorporate more or fewer details in a master equation treatment, which makes the approach flexible. In some cases, we can even solve the master equation directly, while in others we have to resort to numerical solutions.

For the moment, let's focus on a very simple system. Suppose that we have a gas of molecules X with quantum states labeled by a quantum number v . There could of course be many quantum numbers. The point is that we can label individual quantum states, or perhaps just energy levels if the quantum states are degenerate and we have no reason to distinguish between degenerate states. The transitions between quantum states are modeled as a set of chemical reactions:



The rate constants $k_{v \rightarrow v'}$ are called **state-to-state rate constants**. In general, they depend on the temperature, and they can depend on, for example, the concentrations of various

¹The master equation is sometimes said to describe the population of a state. This causes problems in interpretation if the population is small, while the probabilistic interpretation always works.

species in the gas if collisional processes are important. We write down one rate equation for each state. The rate equation for p_v , the probability of occupation of state v , includes terms for all the different ways that this state can gain or lose in probability. Specifically,

$$\frac{dp_v}{dt} = \sum_{v' \neq v} [k_{v' \rightarrow v} p_{v'} - k_{v \rightarrow v'} p_v]. \quad (1)$$

The term ‘master equation’ refers to the full set of these rate equations. The first term in the square braces represents a gain in probability of state v due to transitions from state v' . The second term represents a loss of probability due to transitions from state v to state v' . The equation for p_v contains terms for each state to which or from which direct transitions with state v are possible. There is one of these rate equations for each state of the system. It is not at all unusual for master equations to consist of hundreds or even thousands of equations, each of which may contain just a few terms, or sometimes dozens of terms. Deciding which terms to include and which to leave out usually requires some physical insight, and is the major determinant of how accurate a particular master equation treatment will be in given circumstances.

If you’re wondering about the physical basis of the master equation, imagine multiplying equation 1 by N , the total number of molecules in a large ensemble. Since $Np_v = N_v$, the number of molecules in state v , you can see that equation 1 becomes

$$\frac{dN_v}{dt} = \sum_{v' \neq v} [k_{v' \rightarrow v} N_{v'} - k_{v \rightarrow v'} N_v],$$

which is the mass-action rate equation for N_v , provided the ensemble is sufficiently large that we can treat the number of molecules in each state as a continuous variable. Thus, the master equation gives normal mass-action kinetics in the limit of large N . The master equation is therefore equivalent to a mass-action model for the state-to-state transitions.

2 The Landau-Teller model

In order to solve the master equation, we need to know the state-to-state rate constants. These can either be obtained from experiments or, more often, they derive from some physical model of the excitation/deexcitation processes. The predictions of the master equation for a particular model can then be compared to experiment, which then tells us whether or not the model is an accurate one for a particular situation. Whether the model agrees or disagrees with experiment, we will then have learned something about the processes which cause molecules to gain or lose energy.

Here, we will look at the vibrational relaxation of a gas of harmonic oscillators. In this case, v represents the vibrational quantum number. For harmonic oscillators, collisional energy transfer obeys the selection rule

$$\Delta v = \pm 1. \quad (2)$$

We also assume that

$$k_{v \rightarrow v-1} = vk_{1 \rightarrow 0}, \quad (3)$$

i.e. that the probability of deexcitation is proportional to the quantum number v . These two assumptions together as known as the **Landau-Teller model**. Note that equations 2 and 3 are not arbitrary, but can be derived from first-order perturbation theory of harmonic oscillators.

For the Landau-Teller model, the master equation becomes

$$\frac{dp_v}{dt} = k_{v+1 \rightarrow v} p_{v+1} + k_{v-1 \rightarrow v} p_{v-1} - k_{v \rightarrow v+1} p_v - k_{v \rightarrow v-1} p_v, \quad (4)$$

for $v > 0$, and

$$\frac{dp_0}{dt} = k_{1 \rightarrow 0} p_1 - k_{0 \rightarrow 1} p_0. \quad (5)$$

We have one equation of the form 4 for each value of $v > 0$. For a harmonic oscillator, there is no maximum value of v , so the master equation in this case is in fact an infinite set of differential equations. Don't let that discourage you.

At equilibrium, equation 5 gives

$$k_{1 \rightarrow 0} p_1 = k_{0 \rightarrow 1} p_0. \quad (6)$$

For $v > 0$, the equilibrium condition is

$$k_{v+1 \rightarrow v} p_{v+1} + k_{v-1 \rightarrow v} p_{v-1} = k_{v \rightarrow v+1} p_v + k_{v \rightarrow v-1} p_v. \quad (7)$$

If we set $v = 1$ in equation 7 and use equation 6, we get

$$k_{2 \rightarrow 1} p_2 = k_{1 \rightarrow 2} p_1.$$

We can then use this equation in the equilibrium condition for $v = 2$, and find that a similar equality holds for the $2 \rightleftharpoons 3$ transitions, and so on. Thus, in general,

$$k_{v+1 \rightarrow v} p_{v+1} = k_{v \rightarrow v+1} p_v.$$

This is a **detailed balance condition**. It says that at equilibrium, every individual excitation/deexcitation pair is itself in equilibrium. Rearranging this equation, we get

$$\frac{k_{v \rightarrow v+1}}{k_{v+1 \rightarrow v}} = \frac{p_{v+1}}{p_v}.$$

We know that the equilibrium energy distribution is a Boltzmann distribution. Therefore

$$\frac{p_{v+1}}{p_v} = e^{-\Delta\epsilon/(kT)} = e^{-h\nu/(kT)} \equiv \alpha,$$

where ν is the frequency of the oscillators. Thus,

$$k_{v \rightarrow v+1} = \alpha k_{v+1 \rightarrow v}.$$

Now using the Landau-Teller assumption 3, we get $k_{v+1 \rightarrow v} = (v + 1)k_{1 \rightarrow 0}$ and

$$k_{v \rightarrow v+1} = \alpha(v + 1)k_{1 \rightarrow 0}. \quad (8)$$

Thus in the Landau-Teller model, if we specify any *one* of the state-to-state rate constants, all the others are determined through equations 3 and 8. If we substitute these equations into the Landau-Teller master equation (4 and 5), we get

$$\begin{aligned} \frac{dp_0}{dt} &= k_{1 \rightarrow 0}p_1 - \alpha k_{1 \rightarrow 0}p_0, \\ &= k_{1 \rightarrow 0}(p_1 - \alpha p_0); \end{aligned}$$

and, for $v > 0$,

$$\begin{aligned} \frac{dp_v}{dt} &= (v + 1)k_{1 \rightarrow 0}p_{v+1} + \alpha v k_{1 \rightarrow 0}p_{v-1} - \alpha(v + 1)k_{1 \rightarrow 0}p_v - v k_{1 \rightarrow 0}p_v \\ &= k_{1 \rightarrow 0}[(v + 1)p_{v+1} + \alpha v p_{v-1} - \alpha(v + 1)p_v - v p_v]. \end{aligned}$$

Note that $k_{1 \rightarrow 0}$ is a common factor in each equation of the master equation. This rate constant therefore just sets the relaxation rate. To see this, rewrite

$$\frac{dp_v}{d(k_{1 \rightarrow 0}t)} = (v + 1)p_{v+1} + \alpha v p_{v-1} - \alpha(v + 1)p_v - v p_v.$$

Then define the rescaled time

$$\tau = k_{1 \rightarrow 0}t$$

such that our rate equations for the p_v 's become

$$\frac{dp_0}{d\tau} = p_1 - \alpha p_0, \quad (9)$$

$$\frac{dp_v}{d\tau} = (v + 1)p_{v+1} + \alpha v p_{v-1} - \alpha(v + 1)p_v - v p_v. \quad (10)$$

Physically, using τ instead of t just corresponds to changing our units for time to multiples of $1/k_{1 \rightarrow 0}$. Note that our equations now just depend on a single parameter, namely α . As an illustration, imagine that we take an initially cold system (with $p_0 = 1$ and $p_v = 0$ for all other values of v) and do a temperature jump at $\tau = 0$ to $\alpha = 0.8$ ($\frac{h\nu}{kT} \approx \frac{1}{5}$). Then the master equation will show us how the equilibrium Boltzmann distribution is approached. There's one little catch: We can't solve an infinite set of differential equations.² One way to deal with this is to include all the equations up to some v_{\max} that is large enough so that the probability of that and higher states is negligible, then set $p_{v_{\max}+1} = 0$ to close the system of equations.³ The results of this calculation are shown in figure 1.

²By this I mean that it can't be done numerically, although it is sometimes possible to obtain analytic solutions in special cases.

³There are other ways to deal with this problem. For instance, we can set the terms in $dp_{v_{\max}}/dt$ that correspond to transfer in and out of state $v_{\max} + 1$ equal to zero. This is in some ways a better solution since it guarantees conservation of probability, but in practice, if v_{\max} is large enough and the calculation isn't too long, it doesn't make any difference.

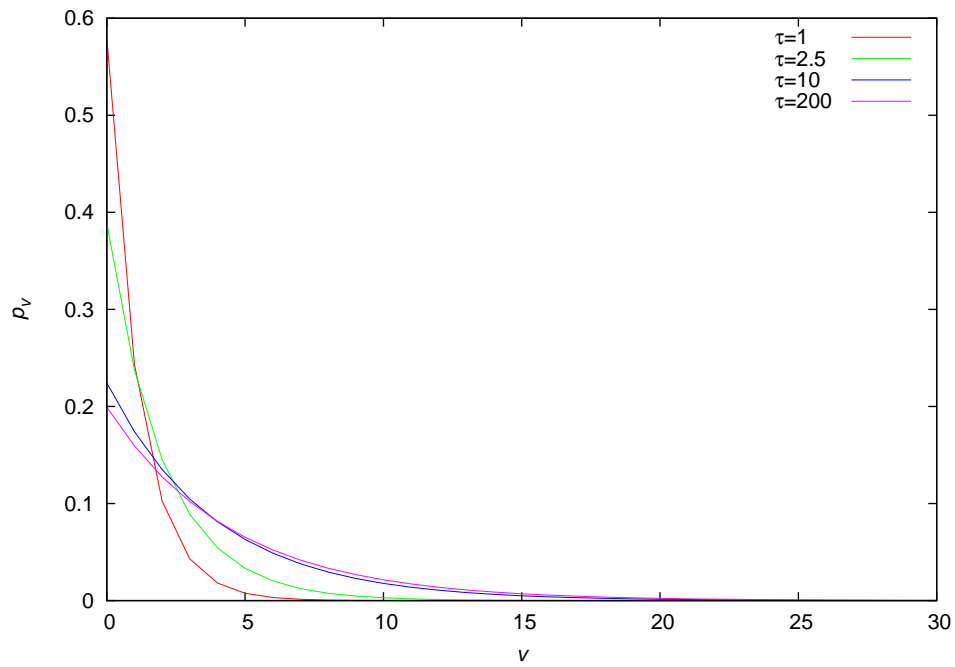


Figure 1: Time evolution of the probability distribution for the Landau-Teller model with $\alpha = 0.8$. The differential equations were integrated with a v_{\max} of 50 and checked with $v_{\max} = 200$. The differences between the two calculations are negligible on the scale of this figure.

3 Other types of master equations

The concept of a master equation is very general. People use this term to describe any system where the probability distribution for a set of discrete states is governed by a set of differential equations representing transfer between these states. Master equations are used particularly when there is a “ladder” of states to climb. Here are some examples:

- Chemical reactions can be treated using the **chemical master equation**. In this case, the states are the possible compositions of the system (expressed in numbers of molecules). For example, in a reaction $A \rightleftharpoons B$, it is enough to know the number of molecules of A since we can then calculate the number of molecules of B given the total number of molecules present. The states are therefore $N_A = 1, 2, 3, \dots, N_{\text{total}}$. The chemical master equation is a set of rate equations for the probabilities $p(N_A, t)$. This idea can be generalized to arbitrary mechanisms. The chemical master equation is particularly useful for describing small chemical systems (e.g. those arising when describing the biochemistry of living cells).
- Master equations have been used to describe polymerization reactions in a few different ways:
 - The polymerization of a single molecule can be described if we write equations for the evolution of the probability that the polymer has n monomers at time t .
 - The states can also be the number of polymers containing n monomers. This case is a specialized version of the chemical master equation.

Exercises

1. Show that the Boltzmann distribution of a harmonic oscillator can be written in the form $p_v = \alpha^v(1 - \alpha)$.
2. Verify that the Boltzmann distribution is an equilibrium solution of equations 9 and 10.