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On the solution of Markovian master equations

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Abstract. For the solution of Markovian master equations a new method is introduced, which is based on a transformation of the original equation for the probability into one for a slowly varying function.

Let N be the particle number of a chemical reacting species. Under Markovian assumption one may derive for the probability $p(N, t)$ the master equation (McQuarrie 1967)

$$\dot{p}(N, t) = -p(N, t)(c^{(+)}(N) + c^{(-)}(N)) + c^{(+)}(N-1)p(N-1, t) + c^{(-)}(N+1)p(N+1, t). \quad (1)$$

We have assumed that there are only changes from N to $N \pm 1$ in each step of reaction. $c^{(+)}(N)$ and $c^{(-)}(N)$ are the corresponding transition probabilities. The steady state distribution of (1) is well known (Landauer 1962) to be

$$p^*(N) = p^*(0) \prod_{\nu=0}^{N-1} \frac{c^{(+)}(\nu)}{c^{(-)}(\nu+1)}. \quad (2)$$

The asterisk designates steady state quantities. (2) is derived from

$$j^*(N) = c^{(+)}(N)p^*(N) - c^{(-)}(N+1)p^*(N+1) = 0 \quad (3)$$

where $j^*(N)$ is the probability flux from N to $N+1$. Therefore distribution (2) is said to be of the detailed balance type.

If we allow for reaction steps from N to $N \pm 2$, in place of (1) we get

$$\begin{aligned} \dot{p}(N, t) = & -p(N, t)(c^{(+)}(N) + c^{(-)}(N) + c^{(++)}(N) + c^{(--)}(N)) \\ & + c^{(+)}(N-1)p(N-1, t) + c^{(-)}(N+1)p(N+1, t) \\ & + c^{(++)}(N-2)p(N-2, t) + c^{(--)}(N+2)p(N+2, t). \end{aligned} \quad (4)$$

$c^{(++)}(N)$ and $c^{(--)}(N)$ are the transition probabilities for the 2-particle reaction steps. Now in general (3) does not hold for the steady state of (4) and no simple construction as (2) is at hand.

A frequently used approximation consists in going over to a continuous variable N and replacing (4) by the Fokker-Planck equation. Examination of this method in the exactly soluble case (1) shows that it can fail essentially for particle numbers well off the peaks of the distribution (Landauer 1962). This becomes important in situations where the heights of two or more peaks have to be compared (Landauer 1962, Janssen 1974).

In place of that we propose to look for equations for the quantity

$$q(N, t) = p(N + 1, t) / p(N, t) \tag{5}$$

from which $p(N, t)$ is obtained to

$$p(N, t) = p(0, t) \prod_{\nu=0}^{N-1} q(\nu, t). \tag{6}$$

In the following we restrict our considerations to slowly varying transition probabilities

$$c^{(i)}(N \pm 1) = c^{(i)}(N) + O(c^{(i)}(N) / \Omega) \quad i = +, -, ++, -- \tag{7}$$

where Ω denotes a dimensionless quantity proportional to the volume of the system. Similarly we assume

$$q^*(N \pm 1) = q^*(N) + O(1 / \Omega). \tag{8}$$

Dividing the steady state equation of (1) by $p^*(N)$, we get, making use of (7) and (8) and dropping the higher order terms,

$$0 = -(c^{(+)}(N) + c^{(-)}(N)) + c^{(+)}(N)q^{*-1}(N) + c^{(-)}(N)q^*(N). \tag{9}$$

This quadratic equation for $q^*(N)$ has the solutions

$$q^*(N) = 1 \quad q^*(N) = c^{(+)}(N) / c^{(-)}(N). \tag{10}$$

The first of these is excluded, because it leads to equipartition over N and thus cannot be normalized. The second one equals the exact result (2) up to terms of the order Ω^{-1} and becomes exact in the thermodynamic limit $\Omega \rightarrow \infty$. The method is not restricted to (1) where detailed balance holds. The steady state distribution of (4) is obtained in analogy to (9) from

$$0 = -(c^{(+)}(N) + c^{(-)}(N) + c^{(++)}(N) + c^{(--)}(N)) + c^{(+)}(N)q^{*-1}(N) + c^{(-)}(N)q^*(N) + c^{(--)}(N)q^{*2}(N) + c^{(++)}(N)q^{*-2}(N). \tag{11}$$

Even if reaction steps changing N by more than 1 or 2 are included, the problem is reduced to an algebraic equation.

From the equation of motion for $p(N, t)$ we can obtain one for $q(N, t)$. Making use of (1) and restricting ourselves to situations with

$$q(N \pm 1, t) = q(N, t) \pm \frac{\partial q}{\partial N}(N, t) + O\left(\frac{1}{\Omega}\right) \\ c^{(i)}(N \pm 1) = c^{(i)}(N) \pm \frac{\partial c^{(i)}}{\partial N}(N) + O\left(\frac{c^{(i)}(N)}{\Omega^2}\right) \quad i = +, - \tag{12}$$

we find

$$\frac{\partial q}{\partial t}(N, t) = \frac{\dot{p}(N + 1, t)}{p(N, t)} - \frac{p(N + 1, t)}{p(N, t)} \frac{\dot{p}(N, t)}{p(N, t)} \\ = -q(N, t) \frac{\partial}{\partial N} (c^{(+)}(N) + c^{(-)}(N) - c^{(+)}(N)q^{-1}(N, t) - c^{(-)}(N)q(N, t)) \tag{13}$$

where $O(c^{(i)}(N) / \Omega^2)$ has been omitted. The solution of this nonlinear partial differential equation gives according to (6) the desired distribution. The basis of (13), the truncated expansion (12) of $q(N \pm 1, t)$ is better justified than one of $p(N \pm 1, t)$, because $q(N, t)$ is

by construction more slowly varying than $p(N, t)$. This is confirmed by the practically exact result in the detailed balance case.

Let $\hat{N}(t)$ be the site of a peak of the distribution. Then we have

$$q(\hat{N}(t), t) = 1. \tag{14}$$

This leads after implicit differentiation and by use of (13) to

$$\frac{d\hat{N}}{dt} = - \frac{(\partial q / \partial t)(\hat{N}, t)}{(\partial q / \partial N)(\hat{N}, t)} = c^{(+)}(\hat{N}) - c^{(-)}(\hat{N}). \tag{15}$$

(15) is a closed equation for the motion of the peaks of the distribution. No assumption of factorization has been made. Near $\hat{N}(t)$ we find

$$q(N, t) \approx 1 + (\partial q / \partial N)(\hat{N}(t), t)(N - \hat{N}(t)) \tag{16}$$

and consequently

$$p(N, t) \approx p(\hat{N}(t), t) \exp\left(\int_{N(t)}^N d\nu \ln q(\nu, t)\right) \\ \approx p(\hat{N}(t), t) \exp[-(N - \hat{N}(t))^2(-(\partial q / \partial N)(\hat{N}(t), t))]. \tag{17}$$

Therefore $(\partial q / \partial N)(\hat{N}(t), t)$ determines the width of the peak at $\hat{N}(t)$ as long as (16) is a good approximation in the region of the peak. Otherwise one has to take into account higher order terms in (16). Putting

$$(\partial q / \partial N)(\hat{N}(t), t) = m(t) \tag{18}$$

we obtain from (13)

$$\frac{dm}{dt} = m \left[(c^{(+)}(\hat{N}(t)) + c^{(-)}(\hat{N}(t)))m - 2 \left(\frac{\partial c^{(+)}}{\partial N}(\hat{N}(t)) - \frac{\partial c^{(-)}}{\partial N}(\hat{N}(t)) \right) \right]. \tag{19}$$

This is a closed equation of motion for the fluctuation around the peak at $\hat{N}(t)$, once $\hat{N}(t)$ is known as solution of (15). Analogous equations for the higher derivatives of q at $\hat{N}(t)$ are found (Kubo *et al* 1973).

In the case of k variables one defines

$$q_l(N_{1,\dots}, N_{k,t}) = p(N_1, \dots, N_{l+1,\dots}, N_{k,t}) / p(N_{1,\dots}, N_{l,\dots}, N_{k,t}) \quad l = 1, \dots, k. \tag{20}$$

The q_l are not independent of each other With (Kubo *et al* 1973)

$$p(N_{1,\dots}, N_{k,t}) = \exp \Psi(N_{1,\dots}, N_{k,t}) \tag{21}$$

we have

$$\ln q_l \approx \partial \Psi / \partial N_l. \tag{22}$$

The steady state equation containing all the q_l becomes a partial differential equation for Ψ . Results corresponding to (13), (15) and (16) can be derived.

Finally it shall be stressed that (13) is not completely equivalent to the original master equation. Taking into account higher order terms in the expansion (12) can be necessary in certain situations.

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