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Master Thesis

Gaussian approximation to the resolution of master equations

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Contents

1 Introduction **3**

2 Stochastic processes **5**

- 2.1 Markovian processes 6
- 2.2 The master equation 7
- 2.3 Methods of solution 8
  - 2.3.1 Generating function 8
  - 2.3.2 Van Kampen's expansion 9
  - 2.3.3 Gillespie method 11

3 The Gaussian approximation **13**

- 3.1 Formulation 13
- 3.2 Error of the method 16

4 Reaction-limited process **19**

5 Autocatalitic reaction **23**

6 Opinion formation **29**

7 Conclusions **35**

8 Appendix1: Reaction-limited process **39**

9 Appendix2: Autocatalitic reaction **45**

1

Introduction

Physicists have been using statistical concepts to describe Nature even before the foundations of Statistical Mechanics were laid out in the late XIX century. Nowadays, Statistical Mechanics is a well developed theory that has been able to relate the macroscopic properties of matter and radiation with their microscopic behavior. This has been most successful in systems at thermal equilibrium where a formal program, that of equilibrium ensembles, can be fully worked out, although in many cases mathematical complexity prevents from finding the actual solution to a given problem.

Very often, when studying systems which are composed by many particles or which interact with the surroundings in an uncontrolled way, a detailed description of the system is not possible. We need then a stochastic formulation of the process. In many cases, even though the microscopic variables evolve in an irregular and unpredictable way, there exists a level of description in which some macroscopic variables follow simple laws. The rest, eliminated, variables, however, make themselves present through fluctuations over the macroscopic behavior. Most often, these fluctuations are negligible and can be ignored. However in some other cases they are important and even dominant in the macroscopic range.

A classical example is the Brownian motion. A heavy particle is immersed in a fluid of light molecules which collide with it in a random fashion. As a consequence, the particle undergoes an erratic movement. It is not possible to describe the (deterministic) motion of all the molecules of the system, however if we focus on the position of the Brownian particle and assign probabilities to its possible displacements after a given time step (during which it suffered many collisions), we are able to derive the probability distribution of the position of the particle in time and from it, the statistical properties of the motion. .This approach can be applied to many situations, especially in systems out of equilibrium where other approaches fail and master equations (differential equations for the evolution in time of the probability) play a prominent role, but are usually very hard to solve.

In this dissertation we review the basic mathematical formalism to describe stochastic processes, and we introduce master equations and some methods of solution. In the second part, we present and analyze a novel method to approximate the solution of a master equation. We apply it to several processes of interest in the literature and compare it with the other presented methods.

2

Stochastic processes

Let us start with some mathematical definitions.

A probability space is defined by a triple $(\Omega, F, \mathtt{P})$, consisting on a space of elementary events Ω, a σ-algebra of events F in Ω and a measure $\mathtt{P}$ defined on F such that $\mathtt{P}(\Omega) = 1$ ($\mathtt{P}$ is called the probability).

A random variable X is an application from the space of elementary events to the real numbers. If the random variable has a continuous one dimensional range (we will assume that in what follows), the probability that X takes a value between x and $x + dx$ is given by $P(x)dx$, where P is a real-valued function such that
$P(x) \geqslant 0$ and $\int dx P(x) = 1$.
$P(x)$ is called the probability density at x.

A stochastic process or random function (Y) is an application from a set (usually the reals or the integers, interpreted as time) and a random variable to the reals. So if X is a random variable, we have:

$$Y_X(t) = f(X, t) \tag{2.1}$$

When X takes one of its possible values (x), the stochastic process (Y) takes another, according to:

$$Y_x(t) = f(x, t)$$

If X is distributed following $P_X(x)$, we can compute the moments of Y:

$$\langle Y_X(t) \rangle = \int dx P_X(x) Y_x(t)$$

$$\langle Y_X(t_1) Y_X(t_2) \ldots Y_X(t_n) \rangle = \int dx P_X(x) Y_x(t_1) Y_x(t_2) \ldots Y_x(t_n)$$

The probability density for $Y_X(t)$ to take the value y at a time t is:

$$P(Y_X(t) = y) \equiv P_1(y, t) = \int dx P_X(x) \delta(Y_x(t) - y)$$

And the joint probability density that Y takes the value y_1 at t_1, y_2 at t_2,..., y_n at t_n:

$$P(Y_X(t_1) = y_1; Y_X(t_2) = y_2; \dots; Y_X(t_n) = y_n) \equiv P_n(y_1, t_1; y_2, t_2; \dots; y_n, tn)$$
$$= \int dx P_X(x)\delta(Y_x(t_2) - y_2) \dots \delta(Y_x(t_n) - y_n)$$

Now we can compute the moments as:

$$\langle Y(t) \rangle = \int dyy P_1(y,t)$$

$$\langle Y(t_1)Y(t_2) \dots Y(t_n) \rangle = \int dy_1 dy_2 \dots dy_n y_1 y_2 \dots y_n P_n(y_1, t_1; y_2, t_2; \dots; y_n, t_n)$$

In general, any hierarchy of functions P_n which obey:
1. $P_n \geqslant 0$
2. P_n is invariant under the change (y_i, t_i) and (y_j, t_j)
3. $\int P_n(y_1, t_1; \dots; y_{n-1}, t_{n-1}; y_n, t_n) dy_n = P_{n-1}(y_1, t_1; \dots; y_{n-1}, t_{n-1})$
4. $\int P_1(y,t) dy = 1$

completely determines a stochastic process $Y(t)$ as defined in (2.1).

In this way, the hierarchy of distribution functions constitutes an alternative definition of a stochastic process. Usually the stochastic variable X with corresponds to a given hierarchy is rather abstract and of little interest in physical applications, and the characterization of the process via the hierarchy of distribution functions is the more common one.

2.1 Markovian processes

The conditional probability densities are defined as:

$$P_{l|n-l}(y_1; t_1; \dots; y_l, t_l | y_{l+1}, t_{l+1}; \dots; y_n, t_n) = \frac{P_n(y_1; t_1; \dots; y_l, t_l; y_{l+1}, t_{l+1}; \dots; y_n, t_n)}{P_{n-l}(y_{l+1}, t_{l+1}; \dots; y_n, t_n)}$$

$P_{l|n-l}(y_1; t_1; \dots; y_l, t_l | y_{l+1}, t_{l+1}; \dots; y_n, t_n)$ represents the probability density that Y takes the values y_1 at t_1,...,y_l at t_l given that it takes the values y_{l+1} at t_{l+1},...,y_n at t_n.

A Markov process is a stochastic process with the property:

$$P_{1|n-1}(y_n, t_n | y_1, t_1; \dots; y_{n-1}, t_{n-1}) = P_{1|1}(y_n, t_n | y_{n-1}, t_{n-1}) \tag{2.2}$$

for any set of n successive times $(t_1 < t_2 < \dots < t_n)$. A Markov process is fully determined by the functions $P_1(y,t)$ and $P_{1|1}(y_2, t_2 | y_1, t_1)$. We can recover the whole hierarchy of probability densities form these two functions:

$$P_n(y_1, t_1; \dots; y_n, t_n) = P_1(y_1, t_1) P_{1|1}(y_2, t_2 | y_1, t_1) P_{1|1}(y_3, t_3 | y_2, t_2) \dots P_{1|1}(y_n, t_n | y_{n-1}, t_{n-1})$$

(for $t_1 < t_2 < \cdots < t_n$).

When the transition probabilities depend on time differences alone, the process is said to be homogeneous.

Now, the function $P_{1|1}(y_1, t_1|y_2, t_1)$ is not arbitrary since:

$$\begin{aligned} P_3(y_1, t_1; y_2, t_2; y_3, t_3) &= P_{2|1}(y_2, t_2; y_3, t_3|y_1, t_1)P_1(y_1, t_1) \\ &= P_{1|1}(y_3, t_3|y_2, t_2)P_{1|1}(y_2, t_2|y_1, t_1)P_1(y_1, t_1) \end{aligned}$$

dividing the right hand sides by $P_1(y_1, t_1)$ and integrating over y_2, we obtain:

$$P_{1|1}(y_3, t_3|y_1, t_1) = \int dy_2 P_{1|1}(y_3, t_3|y_2, t_2)P_{1|1}(y_2, t_2|y_1, t_1) \tag{2.3}$$

This is called the Chapman-Kolmogorov equation and is an identity obeyed by all Markov processes (when $t_1 < t_2 < t_3$).
Any two nonnegative functions P_1 and $P_{1|1}$ that follow the Chapman-Kolmogorov equation and the consistency condition:

$$P_1(y_2, t_2) = \int dy_1 P_{1|1}(y_2, t_2|y_1, t_1)P_1(y_1, t_1)$$

define uniquely a Markov process.

2.2 The master equation

The Chapman-Kolmogorov equation is a functional relation that is not easy to handle in practice. A more convenient form of it and closer to physical concepts, is the master equation, which is a differential form of the Chapman-Kolmogorov equation.

To obtain it, we have to ascertain how $P_{1|1}$ behaves for small time differences (from now on we write P for $P_{1|1}$). We have:

$$P(x, t + \Delta t|y, t) = W(x|y, t)\Delta t + \left(1 - \textstyle\int dv W(v|y, t)\Delta t\right) \delta(x - y) + O(\Delta t^2) \tag{2.4}$$

That is, $W(x|y, t)$ is the probability density per unit of time for the system to go from y to x at time t (the second term represents the probability that the system stays at y during Δt).
Now, using the Chapman-Kolmogorov equation, we can write:

$$\begin{aligned} &P(x, t + \Delta t|z, t') = \textstyle\int dy P(x, t + \Delta t|y, t)P(y, t|z, t') \\ &= \textstyle\int dy \left[W(x|y, t)\Delta t + \left(1 - \int dv W(v|y, t)\Delta t\right) \delta(x - y) + O(\Delta t^2)\right] P(y, t|z, t') \\ &= P(x, t|z, t') + \textstyle\int dy \left[W(x|y, t)P(y, t|z, t') - W(y|x, t)P(x, t|z, t')\right] \Delta t + O(\Delta t^2) \end{aligned}$$

Subtracting $P(x, t|z, t')$, dividing by Δt and taking the limit $\Delta t \to 0$, we obtain:

$$\frac{\partial P(x, t|z, t')}{\partial t} = \int dy \left[W(x|y, t)P(y, t|z, t') - W(y|x, t)P(x, t|z, t')\right] \tag{2.5}$$

This is usually written in a simplified form:

$$\frac{\partial P(x,t)}{\partial t} = \int dy \left[W(x|y,t)P(y,t) - W(y|x,t)P(x,t) \right] \tag{2.6}$$

The meaning of (2.6) is that the solution of this equation with $P(x,t') = \delta(x-z)$ gives the transition probability of the Markov process ($P_{1|1}(x,t|z,t')$) for all $t > t'$ and for any choice of z and t'. It is not meant as an equation for the single time distribution.
However, if we know the initial state of the system, that is, $P_1(x,t_0) = \delta(x-x_0)$, then we have $P_1(x,t) = \int dy P_{1|1}(x,t|y,t_0)P_1(y,t_0) = P_{1|1}(x,t|x_0,t_0)$ and then, the solution of (2.6) with initial condition $P(x,t_0) = \delta(x-x_0)$ gives the single time distribution $P_1(x,t)$ for all $t > t_0$.

If the process has a discrete set of possible states, labeled by n, the master equation reduces to:

$$\frac{\partial P(n,t)}{\partial t} = \sum_{n'} \left[W_{n,n'}(t)P(n',t) - W_{n',n}(t)P(n,t) \right] \tag{2.7}$$

If the process is homogeneous the explicit dependence of t in $W_{n,n'}(t)$ disappears.

2.3 Methods of solution

In the case of a discrete set of states, the master equation is a system of several (usually infinite) coupled first order differential equations, and solving it is often a hard task. There are some methods to approach this problem (usually approximated) and we discuss some of them in the following.

2.3.1 Generating function

The probability generating function ($G(s,t)$) is defined by:

$$G(s,t) = \sum_n s^n P(n,t) \tag{2.8}$$

Clearly, $G(1,t) = 1$, $G(0,t) = P(0,t)$. Moreover, we can obtain the moments of n knowing the derivatives of $G(s,t)$ at $s=1$, for example:

$$\langle n(t) \rangle = \left. \frac{\partial G(s,t)}{\partial s} \right|_{s=1}, \quad \langle n^2(t) \rangle = \left. \frac{\partial^2 G(s,t)}{\partial s^2} \right|_{s=1} + \left. \frac{\partial G(s,t)}{\partial s} \right|_{s=1}$$

Starting with the master equation we can obtain a partial differential equation for the generating function that, in some cases, can be solved. Once we have the expression of $G(s,t)$, expanding it in powers of s we get the probabilities.

Let's apply this technique to the following example.
We consider a population of individuals. Each individual has a probability per unit of time d of dying and there is a probability per unit of time b for a new individual to enter in the population (we consider it independent of the number of individuals for simplicity). This is known as the birth and death process. Its master equation is given by:

$$\frac{\partial P(n,t)}{\partial t} = d(n+1)P(n+1,t) + bP(n-1,t) - (dn+b)P(n,t) \tag{2.9}$$

This is equivalent to (2.7) setting $W_{n,n'}(t) = dn'\delta_{n',n+1} + b\delta_{n',n-1}$.
Multiplying both sides of (2.9) by s^n and summing over all values of n, we get:

$$\frac{\partial G(s,t)}{\partial t} = d(1-s)\frac{\partial G}{\partial s} + b(s-1)G(s,t) \tag{2.10}$$

This partial differential equation can be solved by the Lagrange method, and its solution with initial condition $G(s,0) = s^N$ (which comes from $P(n,0) = \delta_{n,N}$) is:

$$G(s,t) = e^{\frac{b}{d}(s-1)(1-e^{-dt})}\left(se^{-dt} + 1 - e^{-dt}\right)^N$$

Expanding $G(s,t)$ in powers of s we get the probabilities $P(n,t)$.It's expression is rather complicated in the time-dependent case, but gets much simplified in the stationary ($t \to \infty$) case, when we have:

$$G(s, t \to \infty) = e^{\frac{b}{d}(s-1)}$$

$$P(n, t \to \infty) = \frac{e^{-b/d}}{n!}\left[\tfrac{b}{d}\right]^n \tag{2.11}$$

a Poisson distribution with parameter $\frac{b}{d}$.

As we have seen, using the generating function we transform a set of coupled first order differential equations into a single partial differential equation. However, in many cases (when $W_{n,n'}$ are nonlinear functions of n') the equation obtained is a high order partial differential equation with nonconstant coefficients and its general solution is not known. In this cases approximated methods are needed.

2.3.2 Van Kampen's expansion

In many cases the master equation depends on a large parameter, Ω, (usually the system size or volume) and the evolution of the system becomes deterministic as this parameter goes to infinity. In this cases a systematic expansion of the master equation in powers of $\Omega^{-1/2}$ is possible.

The expansion is based on the existence of two different scales. On one hand the macroscopic properties of the system are functions of the intensive variable x/Ω, so that we expect that the probability for a transition to take place depends on this variable i. e. as Ω varies the probability remains the same function of x/Ω. On the other hand, the size of the transition jumps are function of the extensive variable x. Formally, it is assumed that we can write the transition probabilities as:

$$W_\Omega(x|y) = f(\Omega)\left[\Phi_0(\tfrac{y}{\Omega}, x-y) + \Omega^{-1}\Phi_1(\tfrac{y}{\Omega}, x-y) + \Omega^{-2}\Phi_2 + ...\right] \tag{2.12}$$

For concreteness, we are going to consider a master equation with discrete states of the form:

$$\frac{\partial P(n,t)}{\partial t} = \sum_{k=-\infty}^{\infty} (E^k - 1)\left[\frac{G_k(n)}{\Omega^{g_k-1}} P(n,t)\right] \tag{2.13}$$

where G_k is a polynomial in n of degree g_k and E is a linear operator such that $E\left[f(n)\right] = f(n+1)$. Note that the transition probabilities follow the assumption (2.12). In most of the cases one meets in practice the master equation can be written in this general form.

Next, the following ansatz is formulated:

$$n = \Omega\phi(t) + \Omega^{1/2}\xi \tag{2.14}$$

with $\phi, \xi \sim O(\Omega^0)$. This means that the stochastic variable n has a macroscopic component of order Ω and a fluctuating part of order $\Omega^{1/2}$. This ansatz is the essential step of the expansion and is justified because we will find that $P(n,t)$, when expressed in ξ, does not depend on Ω to first approximation.

Now we proceed performing the time-dependent change of variables from n to ξ in the master equation (2.13) and expanding in powers of Ω. We obtain:

$$\frac{\partial \Pi(\xi,t)}{\partial t} = \Omega^{1/2}\frac{d\phi}{dt}\frac{\partial \Pi}{\partial \xi} + \sum_{k=-\infty}^{\infty}\left(k\Omega^{-1/2}\frac{\partial}{\partial \xi} + \frac{k^2}{2}\Omega^{-1}\frac{\partial^2}{\partial \xi^2} + ...\right)\left(\frac{G_k(\Omega\phi + \Omega^{1/2}\xi)}{\Omega^{g_k-1}}\Pi\right) \tag{2.15}$$

where $\Pi(\xi,t) = P(\Omega\phi(t) + \Omega^{1/2}\xi, t)$.

The terms of order $\Omega^{1/2}$ vanish if we choose $\phi(t)$ to satisfy:

$$\frac{d\phi}{dt} = -\sum_{k=-\infty}^{\infty} k a_{g_k}\phi^{g_k} \tag{2.16}$$

This is the macroscopic equation. Next, the terms of order Ω^0 give:

$$\frac{\partial \Pi}{\partial t} = \frac{\partial}{\partial \xi}\left[\left(\sum_{k=-\infty}^{\infty} k g_k a_{g_k}\phi^{g_k-1}\right)\xi\Pi\right] + \frac{1}{2}\frac{\partial^2}{\partial \xi^2}\left[\left(\sum_{k=-\infty}^{\infty} k^2 a_{g_k}\phi^{g_k}\right)\Pi\right] \tag{2.17}$$

This is a linear Fokker-Planck equation whose coefficients depend on t through $\phi(t)$. Its solution is a Gaussian distribution and therefore is fully determined by the first two moments, which follow:

$$\frac{d\langle\xi\rangle}{dt} = -\sum_{k=-\infty}^{\infty} k g_k a_{g_k}\phi^{g_k-1}\langle\xi\rangle \tag{2.18}$$

$$\frac{d\langle\xi^2\rangle}{dt} = \sum_{k=-\infty}^{\infty} \left(-2kg_k a_{g_k}\phi^{g_k-1}\langle\xi^2\rangle + k^2 a_{g_k}\phi^{g_k}\right) \tag{2.19}$$

The equations for $\langle\xi(t)\rangle$ and$\langle\xi^2(t)\rangle$ are linear and uncoupled, so they can be solved analytically, provided that we can solve the macroscopic equation for $\phi(t)$ which in general is nonlinear.
If higher order terms are included in (2.17) the Gaussian character is lost. However, these corrections are of order $\Omega^{-1/2}$ and can be neglected in a first approximation.

We propose another (maybe simpler) way to obtain the equations for $\langle\xi(t)\rangle$and $\langle\xi^2(t)\rangle$ that consists on writing the exact equations for $\langle n(t)\rangle$ and $\langle n^2(t)\rangle$ from (2.13), change variables to ξ and expand in powers of Ω. If we consider a change of variables of the form $n = \Omega^a\phi(t)+\Omega^b\xi$, the only values for a and b consistent with $\phi, \xi \sim O(\Omega^0)$ are $a = 1$, $b = \frac{1}{2}$, as expected.

2.3.3 Gillespie method

An exact (in the sense of not biased) numerical algorithm for simulating realizations of an homogeneous Markovian process was proposed by Gillespie [5].
The method is based on the fact that the rate at which the several possible individual transitions happen is fixed as long as the state of the system does not change.

If there are k possible transitions and w_i is the rate at which the transition i takes place, the time at which this transition will actually happen is distributed according to: $P(t_i = t) = w_i e^{-w_i t}$. The time ($\tau$) at which the first transition takes place is the minimun of those times and is, then, distributed according to:

$$P(\tau = t) = \sum_{i=1}^{k} P(t_i = t)\prod_{j\neq i} P(t_j \geq t) = \sum_{i=1}^{k} w_i e^{-w_i t} e^{\sum_{j\neq i} -w_j t} = w_{tot} e^{-w_{tot} t}$$

with $w_{tot} = \sum_{i=1}^{k} w_i$.
We have used the fact that the individual transitions are independent, and neglected the probability of several simultaneous transitions.
In the case of the birth and death process commented in a previous section, there are two possible transitions:
(1) Birth of and individual at a rate b, (2) death of an individual at a rate nd (n being the number of alive individuals).
Once we know when the first transition will take place, we need to know which transition will it be. The probability for each transition is proportional to its rate w_i.

The Gillespie algorithm, then, works as follows:
1. Compute the transition rates, ω_i, (which depend on the state of the system) and the total rate, $w_{tot} = \sum_{i=1}^{k} w_i$.

2. Obtain the time, τ, at which a transition takes place, from a random number distributed following $P(\tau = t) = w_{tot}e^{-w_{tot}t}$. This can be calculated from $\tau = -\frac{1}{w_{tot}}log(u)$, with u a random number uniformly distributed between 0 and 1
3. Establish which transition takes place, each of them having a probability proportional to it's rate.
4. Update the state of the system according to the transition chosen, and the time adding the value τ.
Go back to 1.

We can go from 4 to 1 because the exponential distribution obeys:

$$P(t = \tau | t > \tau_0) = P(t = \tau - \tau_0)$$

so after a given transition the probability for any other transition to take place is again exponentially distributed with time origin in the current time.

To obtain mean values of arbitrary functions we can perform M different realizations of the process via this method and average the corresponding results. The error in the averages obtained in this way decays as $M^{-1/2}$, so when high accuracy is needed the method can be slow.

3

The Gaussian approximation

We propose an approximated method to obtain the average and variance of a stochastic process that follows a master equation. The method is based on ideas coming form van Kampen's expansion approach (the fact that the probability distribution is Gaussian at first order), but it is not completely equivalent to it. We analyze the error introduced and compare with van Kampen's method.

3.1 Formulation

We consider a general master equation of the form:

$$\frac{\partial P(n,t)}{\partial t} = \sum_{k=-\infty}^{\infty} (E^k - 1)\left[\frac{G_k(n)}{\Omega^{g_k-1}} P(n,t)\right] \tag{3.1}$$

where G_k is a polynomial in n of degree g_k, E is a linear operator such that $E(f(n)) = f(n+1)$ and Ω is a large parameter of the system (typically the system size).
Equations of this form appear on the description of chemical reactions, ecological systems and opinion dynamics among other examples.
From (3.1), after some algebra, we can get the exact equations for the moments, defined as $\langle n^m \rangle = \sum_{n=-\infty}^{\infty} n^m P(n,t)$:

$$\frac{d\langle n^m \rangle}{dt} = \sum_{k=-\infty}^{\infty} \frac{1}{\Omega^{g_k-1}} \langle [(n-k)^m - n^m] G_k(n) \rangle \tag{3.2}$$

Particular cases are:

$$\frac{d\langle n \rangle}{dt} = \sum_{k=-\infty}^{\infty} \frac{(-k)}{\Omega^{g_k-1}} \langle G_k(n) \rangle \tag{3.3}$$

$$\frac{d\langle n^2 \rangle}{dt} = \sum_{k=-\infty}^{\infty} \frac{1}{\Omega^{g_k-1}} \langle (k^2 - 2kn) G_k(n) \rangle \tag{3.4}$$

If $G_k(n)$ is not linear (degree greater than 1) for some k, then the equation for each moment depends on higher order ones, so we get an infinite system of coupled differential equations.
The approximation proposed here consists on assuming that the distribution $P(n,t)$ is Gaussian so all the moments can be expressed as a function of the first two and in this way we can get a closed system of equations for $\langle n(t)\rangle$ and $\langle n^2(t)\rangle$. This assumption is not arbitrary because, as we saw in the previous chapter, the van Kampen's expansion [1] method shows that, for a master equation of this form, the probability distribution is Gaussian except for corrections of order $\Omega^{-1/2}$.
In the approximation proposed we have:

$$\frac{d\langle n\rangle}{dt} = \sum_{k=-\infty}^{\infty} \frac{(-k)}{\Omega^{g_k-1}} \langle G_k(n)\rangle_G \tag{3.5}$$

$$\frac{d\langle n^2\rangle}{dt} = \sum_{k=-\infty}^{\infty} \frac{1}{\Omega^{g_k-1}} \langle (k^2-2kn)G_k(n)\rangle_G \tag{3.6}$$

where $\langle n^k\rangle_G$ denotes the expression of $\langle n^k\rangle$ as a function of $\langle n\rangle$ and $\langle n^2\rangle$ that holds for Gaussian probability distributions:

$$\langle n^k\rangle_G = \langle(\overline{n}+\langle n\rangle)^k\rangle_G = \sum_{m=0}^{k} \binom{k}{m} \langle \overline{n}^{k-m}\rangle_G \langle n\rangle^m$$

and

$$\langle \overline{n}^{k-m}\rangle_G = \begin{cases} (k-m-1)!!\langle\overline{n}^2\rangle^{(k-m)/2} = (k-m-1)!!(\langle n^2\rangle - \langle n\rangle^2)^{(k-m)/2} & \text{if} \quad k-m \text{ even} \\ 0 & \text{if} \quad k-m \text{ odd} \end{cases}$$

with $(m')!! \equiv m'(m'-2)(m'-4)....$

So we have:

$$\langle n^{2k}\rangle_G = \sum_{m=0}^{k} \binom{2k}{2m} \langle n\rangle^{2m}(2k-2m-1)!! \sum_{l=0}^{k-m} \binom{k-m}{l} \langle n^2\rangle^{k-m-l}\langle n\rangle^{2l}(-1)^l \tag{3.7}$$

$$\langle n^{2k+1}\rangle_G = \sum_{m=0}^{k} \binom{2k+1}{2m+1} \langle n\rangle^{2m+1}(2k-2m-1)!! \sum_{l=0}^{k-m} \binom{k-m}{l} \langle n^2\rangle^{k-m-l}\langle n\rangle^{2l}(-1)^l$$

The expression of the firsts Gaussian moments are shown in table 3.1.

The Gaussian approximation for obtaining the first moments from a master equation of the form (3.1) proceeds as follows:
1. Compute the exact evolution equations for $\langle n(t)\rangle$ and $\langle n^2(t)\rangle$, (3.3) (3.4).

2. Whenever a higher order moment appears, substitute it with its Gaussian approximation (table 3.1)
3. Solve the system of two coupled first order differential equations.

Moment	Gaussian approximation
$\langle n^3\rangle$	$\langle n^3\rangle_G = 3\langle n^2\rangle\langle n\rangle - 2\langle n\rangle^3$
$\langle n^4\rangle$	$\langle n^4\rangle_G = 3\langle n^2\rangle^2 - 2\langle n\rangle^4$
$\langle n^5\rangle$	$\langle n^5\rangle_G = 15\langle n^2\rangle^2\langle n\rangle - 20\langle n^2\rangle\langle n\rangle^3 + 6\langle n\rangle^5$
$\langle n^6\rangle$	$\langle n^6\rangle_G = 15\langle n^2\rangle^3 - 30\langle n^2\rangle\langle n\rangle^4 + 45\langle n\rangle^6$

Table 3.1: Gaussian moments

This approach is easily generalizable to master equations with several variables. In the case of two variables, and with a master equation of the following form:

$$\frac{\partial P(n_1,n_2,t)}{\partial t} = \sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}(E_1^k E_2^l - 1)\left[\frac{G_{k,l}(n_1,n_2)}{\Omega^{g_{k,l}-1}}P(n_1,n_2,t)\right] \tag{3.8}$$

The equations of evolution for the moments are:

$$\frac{d\langle n_i\rangle}{dt} = \sum_{k_1=-\infty}^{\infty}\sum_{k_2=-\infty}^{\infty}\frac{(-k_i)}{\Omega^{g_{k_1,k_2}-1}}\left\langle G_{k_1,k_2}(n_1,n_2)\right\rangle_G \tag{3.9}$$

$$\frac{d\langle n_i^2\rangle}{dt} = \sum_{k_1=-\infty}^{\infty}\sum_{k_2=-\infty}^{\infty}\frac{1}{\Omega^{g_{k_1,k_2}-1}}\left\langle (k_i^2 - 2k_i n_i)G_{k_1,k_2}(n_1,n_2)\right\rangle_G \tag{3.10}$$

$$\frac{d\langle n_1 n_2\rangle}{dt} = \sum_{k_1=-\infty}^{\infty}\sum_{k_2=-\infty}^{\infty}\frac{1}{\Omega^{g_{k_1,k_2}-1}}\left\langle (k_1k_2 - k_2n_1 - k_1n_2)G_{k_1,k_2}(n_1,n_2)\right\rangle_G \tag{3.11}$$

(i=1,2)

In this case we assume that the joint distribution $P(n_1,n_2)$ is Gaussian, so all higher moments can be expressed as a function of $\langle n_i\rangle$, $\langle n_i^2\rangle$, $\langle n_1n_2\rangle$. We can compute the successive values using Wick's theorem. In table (3.2) we write the expression of the firsts terms.

Moment	Gaussian approximation
$\langle n_1^2n_2\rangle$	$\langle n_1^2\rangle\langle n_2\rangle + 2\langle n_1\rangle\langle n_1n_2\rangle - 2\langle n_1\rangle^2\langle n_2\rangle$
$\langle n_1^2n_2^2\rangle$	$\langle n_1^2\rangle\langle n_2^2\rangle + 2\langle n_1n_2\rangle^2 - 2\langle n1\rangle^2\langle n2\rangle^2$
$\langle n_1^3n_2\rangle$	$3\langle n_1^2\rangle\langle n_1n_2\rangle - 2\langle n1\rangle^3\langle n2\rangle$
$\langle n_1^3n_2^2\rangle$	$6\langle n_1n_2\rangle^2\langle n_1\rangle + 6\langle n1\rangle^3\langle n2\rangle^2 + 6\langle n_1n2\rangle\langle n_2\rangle(\langle n_1\rangle^2 - 2\langle n_1\rangle^2$ $-6\langle n_1^2\rangle\langle n_2\rangle^2\langle n_1\rangle + 3\langle n_1^2\rangle\langle n_2^2\rangle\langle n_1\rangle - 2\langle n_1\rangle^3\langle n_2^2\rangle$

Table 3.2: Gaussian moments with 2 variables

3.2 Error of the method

Using the ansatz employed in van Kampen's expansion: $n = \Omega\phi + \Omega^{\frac{1}{2}}\xi$, we can write:

$$\begin{aligned}
\frac{\langle n\rangle^{2(m+l)}\langle n^2\rangle^{k-m-l}}{\Omega^{2k-1}} &= \Omega\phi^{2k} + \Omega^{1/2}\phi^{2k-1}2k\langle\xi\rangle + \Omega^0\phi^{2k-2}(2k^2-2k+m+l)\langle\xi\rangle^2 \\
&\quad +(k-m-l)\langle\xi^2\rangle + O(\Omega^{-1/2}) \\
&= f_1(k,m) + l f_2(k,m) + O(\Omega^{-1/2})
\end{aligned}$$

Inserting this into (3.7) and taking into account that:

$$\sum_{l=0}^{k-m}\binom{k-m}{l}(-1)^l = (1-1)^{k-m} = \delta_{k,m}$$

$$\sum_{l=0}^{k-m}\binom{k-m}{l}l(-1)^l = -\partial_b((a-b)^{k-m})|_{a=b=1} = -\delta_{k-1,m}$$

we get

$$\begin{aligned}
\frac{\langle n^{2k}\rangle_G}{\Omega^{2k-1}} &= \sum_{m=0}^{k}\binom{2k}{2m}(2k-2m)!![(\Omega\phi^{2k} + \Omega^{1/2}\phi^{2k-1}2k\langle\xi\rangle + \phi^{2k-2}(2k^2-k)\langle\xi\rangle^2)\delta_{k,m} \\
&\quad -\langle\xi\rangle^2\delta_{k-1,m} + \langle\xi^2\rangle\delta_{k-1,m}] + O(\Omega^{-1/2}) \\
&= \Omega\phi^{2k} + \Omega^{1/2}\phi^{2k-1}2k\langle\xi\rangle + \tbinom{2k}{2}\langle\xi^2\rangle + O(\Omega^{-1/2}) = \frac{\langle n^{2k}\rangle}{\Omega^{2k-1}} + O(\Omega^{-1/2})
\end{aligned}$$

Similar calculation can be performed for odd exponent, and we finally have the general result:

$$\frac{\langle n^k\rangle_G}{\Omega^{k-1}} = \frac{\langle n^k\rangle}{\Omega^{k-1}} + O(\Omega^{-1/2}) \tag{3.12}$$

From (3.12) we see that the error we introduce in the equations for the moments when performing the Gaussian approximation (3.5 and 3.6) is of order $O(\Omega^{-1/2})$ for $\langle n\rangle$ and $O(\Omega^{1/2})$ for $\langle n^2\rangle$. So we have:

$$\frac{d\langle n\rangle}{dt} = f_1(\langle n\rangle, \langle n^2\rangle) + O(\Omega^{-1/2}) \tag{3.13}$$

$$\frac{d\langle n^2\rangle}{dt} = f_2(\langle n\rangle, \langle n^2\rangle) + O(\Omega^{1/2}) \tag{3.14}$$

$$\frac{d\langle n\rangle_G}{dt} = f_1(\langle n\rangle_G, \langle n^2\rangle_G) \tag{3.15}$$

$$\frac{d\langle n^2\rangle_G}{dt} = f_2(\langle n\rangle_G, \langle n^2\rangle_G) \tag{3.16}$$

where $f_{1(2)}$ is the right hand side of equation 3.5(3.6), and $\langle n\rangle_G$, $\langle n^2\rangle_G$ denotes the value of the moments obtained performing the Gaussian approximation.

Defining the errors as:
$\langle n\rangle = \langle n\rangle_G + \epsilon_n$, $\langle n^2\rangle = \langle n^2\rangle_G + \epsilon_{n^2}$
And using equations (3.13)-(3.16) we get:

$$\frac{d\epsilon_n}{dt} = \frac{\partial}{\partial\langle n\rangle} f_1(\langle n\rangle_G, \langle n^2\rangle_G)\epsilon_n + \frac{\partial}{\partial\langle n^2\rangle} f_1(\langle n\rangle_G, \langle n^2\rangle_G)\epsilon_{n^2} + (\Omega^{-1/2}) \tag{3.17}$$

$$\frac{d\epsilon_{n^2}}{dt} = \frac{\partial}{\partial\langle n\rangle} f_2(\langle n\rangle_G, \langle n^2\rangle_G)\epsilon_n + \frac{\partial}{\partial\langle n^2\rangle} f_2(\langle n\rangle_G, \langle n^2\rangle_G)\epsilon_{n^2} + (\Omega^{1/2}) \tag{3.18}$$

In this equations we can neglect higher order terms if $\epsilon_n \sim O(\Omega^a)$,$\epsilon_{n^2} \sim O(\Omega^b)$ with $a < 1$, $b < 2$, since $\partial_{\langle n\rangle} \sim O(\Omega^{-1})$, $\partial_{\langle n^2\rangle} \sim O(\Omega^{-2})$. Taking into account that $f_1 \sim O(\Omega)$, $f_2 \sim O(\Omega^2)$, we have:

$$\frac{d\epsilon_n}{dt} = O(\Omega^0)\epsilon_n + O(\Omega^{-1})\epsilon_{n^2} + O(\Omega^{-1/2}) \tag{3.19}$$

$$\frac{d\epsilon_{n^2}}{dt} = O(\Omega)\epsilon_n + O(\Omega^0)\epsilon_{n^2} + O(\Omega^{1/2}) \tag{3.20}$$

If we set $\epsilon_n \sim O(\Omega^a)$, $\epsilon_{n^2} \sim O(\Omega^b)$, equations (3.19), (3.20) imply $b = a + 1 \geqslant 1/2$. If the initial conditions are known, initially $\epsilon_n = \epsilon_{n^2} = 0$ and this equations make $\epsilon_n \sim O(\Omega^{-1/2})$, $\epsilon_{n^2} \sim O(\Omega^{1/2})$. This scaling is then respected by equations (3.19), (3.20).

In conclusion, when performing the Gaussian approximation we get $\langle n\rangle + O(\Omega^{-1/2})$, $\langle n^2\rangle + O(\Omega^{1/2})$, $\sigma^2 + O(\Omega^{1/2})$.
In first order van Kampen's expansion we obtain $\langle\xi\rangle + O(\Omega^{-1/2})$ and $\langle\xi^2\rangle + O(\Omega^{-1/2})$, and from them $\langle n\rangle + O(\Omega^0)$, $\langle n^2\rangle + O(\Omega^{1/2})$, $\sigma^2 + O(\Omega^{1/2})$. So the error in the Gaussian approximation is of smaller order than the error in first order van Kampen's expansion, as we see in table (3.3).

	Error in $\langle n\rangle$	Error in σ^2
1^{st} order van Kampen's expansion	$O(\Omega^0)$	$O(\Omega^{1/2})$
Gaussian approximation	$O(\Omega^{-1/2})$	$O(\Omega^{1/2})$

Table 3.3: Order of the methods

4

Reaction-limited process $A + B \to 0$

In this and the following chapters we will compare the Gaussian approximation presented here with the first order van Kampen's expansion in some specific examples.

Chemical reactions are suitable processes for a stochastic description. The stochastic approach is specially necessary when the number of molecules considered is small, because in this case fluctuations can be very important.
We start with the reaction $A + B \to 0$ (reaction limited process). The master equation describing this process is:

$$\frac{\partial P(n,t)}{\partial t} = \frac{\kappa}{\Omega}\big[(n+1)(\Delta+n+1)P(n+1,t) - n(n+\Delta)P(n,t)\big] \tag{4.1}$$

Where n is the number of particles of specie A, $\Delta = \Omega\delta$ is the difference of the number of particles of type A and B (conserved in the process), κ is the rate at which the reaction is produced and Ω is the volume of the system.
Note that this equation can be written in the form (3.1) setting $G_k(n) = \delta_{k,1}n(n+\Delta)$. In this case $G_k(n)$ depends explicitly on Ω ($G_1(n) = n(n+\Omega\delta)$) so this has to be taken into account when performing van Kampen's expansion, and expressions (2.18), (2.19) are not directly applicable. However this fact does not affect the Gaussian approximation, expressions (3.5) and (3.6) are directly applicable and the error introduced is again of order $\Omega^{-1/2}$ because $\langle\frac{n^3}{\Omega^2} + \frac{\Omega n^2}{\Omega^2}\rangle = \langle\frac{n^3}{\Omega^2} + \frac{\Omega n^2}{\Omega^2}\rangle_G + O(\Omega^{-1/2})$, as we see from (3.12).
This master equation can be solved exactly using the generating function technique, so we will compare the results obtained from the Gaussian approximation an the first order van Kampen's expansion with the exact results.
The exact solution is given by:

$$P(n,t) = \sum_{k=n}^{M} C_k(\Delta, M)B_{n,k}(\Delta)e^{-k(k+\Delta)\kappa t/\Omega} \tag{4.2}$$

with $C_k(\Delta, M) = (-1)^k\frac{2k+\Delta}{k+\Delta}\frac{(k+1)_\Delta}{\Delta!}\frac{(M-k+1)_k}{(M+\Delta+1)_k}$, $B_{n,k}(\Delta) = \frac{(-k)_n(k+\Delta)_n}{n!(\Delta+1)_n}$.

M is the initial number of A particles and $(a)_n$ is the Pochhammer's symbol: $(a)_n = \dfrac{\Gamma(a+n)}{\Gamma(a)}$, or $(a)_n = a(a+1)...(a+n-1)$
Details of the calculation in this and in a more general case are given in appendix1.

From (4.1) we can get the exact expression for the first two moments:

$$\begin{aligned} \langle n(t)\rangle &= \sum_{k=1}^{M}(2k+\Delta)\frac{(M-k+1)_k}{(M+\Delta+1)_k}e^{-k(k+\Delta)\kappa t/\Omega} && (4.3)\\ \langle n^2(t)\rangle &= \sum_{k=1}^{M}(2k+\Delta)(k^2+(k-1)\Delta)\frac{(M-k+1)_k}{(M+\Delta+1)_k}e^{-k(k+\Delta)\kappa t/\Omega} && (4.4)\end{aligned}$$

Using the Gaussian approximation, the evolution equations for the moments are:

$$\begin{aligned} \frac{d\langle n\rangle}{dt} &= -\frac{\kappa}{\Omega}(\langle n^2\rangle+\Delta\langle n\rangle) && (4.5)\\ \frac{d\langle n^2\rangle}{dt} &= \frac{\kappa}{\Omega}(4\langle n\rangle^3-6\langle n^2\rangle\langle n\rangle+(1-2\Delta)\langle n^2\rangle+\Delta\langle n\rangle) && (4.6)\end{aligned}$$

And the first order van Kampen's expansion gives:

$$\begin{aligned} \frac{d\langle\phi\rangle}{dt} &= -\kappa\phi(\phi+\delta)\rightarrow\phi(t)=\frac{\delta\phi_0}{\delta e^{\delta\kappa t}+\phi_0(e^{\delta\kappa t}-1)} && (4.7)\\ \frac{d\langle n\rangle}{dt} &= \kappa\Omega\phi^2-\kappa(\delta+2\phi)\langle n\rangle\rightarrow\langle n(t)\rangle=\delta\frac{\delta e^{\delta\kappa t}\langle n\rangle_0+\phi_0^2\Omega(e^{\delta\kappa t}-1)}{(\phi_0-e^{\delta\kappa t}(\delta+\phi_0))^2} && (4.8)\\ \frac{d\langle n^2\rangle}{dt} &= -2\kappa(2\phi+\delta)\langle n^2\rangle-2\kappa\Omega\phi(\phi+\delta)\langle n\rangle+2\kappa\Omega^2\phi^2(2\phi+\delta)+\kappa\Omega\phi(\phi+\delta)\\ &\rightarrow\langle n^2(t)\rangle=\delta\frac{\Omega e^{3\delta\kappa t}\phi_0(\delta+\phi_0)^3+\Omega^2\delta\phi^4-\Omega(1+2\delta\Omega)e^{\delta\kappa t}\phi_0^3(\delta+\phi_0)}{[\phi_0-e^{\delta\kappa t}(\delta+\phi_0)]^4}\\ &+\frac{\delta^2e^{2\delta\kappa t}[\delta^2\langle n^2\rangle_0-\Omega\delta^2\phi_0-3\Omega\delta\phi_0^2-2\Omega\phi_0^3+2\Omega^2\delta\phi_0^3+\Omega^2\phi_0^4]}{[\phi_0-e^{\delta\kappa t}(\delta+\phi_0)]^4}\\ &-\frac{\delta^2e^{2\delta\kappa t}2\Omega\kappa\phi_0(\delta+\phi_0)[(\langle n\rangle_0-\Omega\phi_0)\delta^2+\delta\phi_0+\phi_0^2]t}{[\phi_0-e^{\delta\kappa t}(\delta+\phi_0)]^4} && (4.9)\end{aligned}$$

In the next figures we compare the exact results with those obtained from the Gaussian approximation (computed by numerical integration of equations 4.5, 4.6) and van Kampen's expansion (equations 4.8, 4.9).

The figures show that the Gaussian approximation reproduces better the exact results for the mean value, an also slightly better for the fluctuations. Increasing Ω (the system size) leads to smaller differences between the approximations and the exact results, as expected. A systematic study of the dependence of the error with Ω is left for the next example.

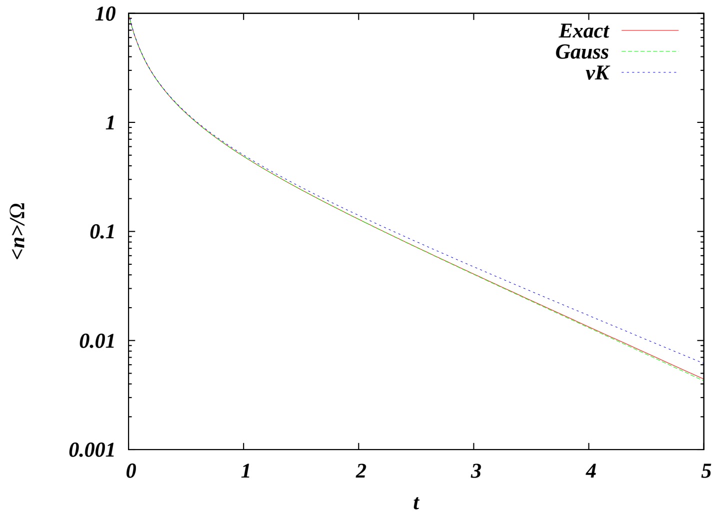

Figure 4.1. $\langle n(t)\rangle/\Omega$ for $\delta = 1, \kappa = 1, M = 100$ and $\Omega = 10$.
Gaussian approximation (green) is almost indistinguishable from the exact result (red).

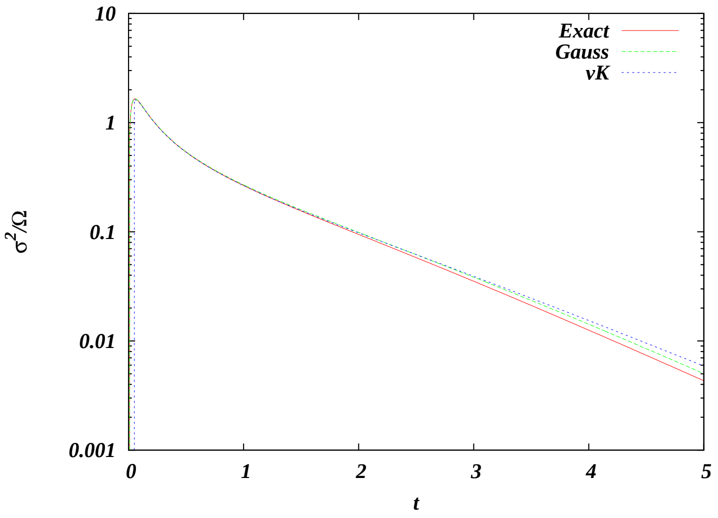

Figure 4.2. Normalized fluctuation σ^2/Ω for $\delta = 1, \kappa = 1, M = 100$ and $\Omega = 10$.
Gaussian approximation (green) is again closer to the exact result (red) than van Kampen's expansion (blue).

5

Autocatalitic reaction $A \to X$, $2X \to B$

The master equation describing this process is:

$$\frac{\partial P(n,t)}{\partial t} = \Omega\phi_A k(P(n-1,t)-P(n,t))+\frac{k'}{\Omega}[(n+2)(n+1)P(n+2,t)-n(n-1)P(n,t)] \tag{5.1}$$

This equation can be written in the form (3.1) setting $G_l(n) = \delta_{l,-1}k\phi_A + \delta_{l,2}k'n(n-1)$.
The general solution for this equation is not known, but the stationary solution ($P^{st}(n)$, obtained setting $\frac{\partial P(n,t)}{\partial t} = 0$) can be obtained using the generating function technique and reads:

$$P^{st}(n) = \frac{(kn_A\Omega/k')^{n/2} I_{n-1}(2\sqrt{kn_A\Omega/k'})}{n!\sqrt{2}I_1(2\sqrt{2kn_A\Omega/k'})} \tag{5.2}$$

where I_n denotes a modified Bessel function. Details are given in appendix 2.

The exact equations for the first moments are:

$$\frac{d\langle n\rangle}{dt} = \Omega k\phi_A + 2k'\frac{\langle n\rangle}{\Omega} - 2k'\frac{\langle n^2\rangle}{\Omega} \tag{5.3}$$

$$\frac{d\langle n^2\rangle}{dt} = \Omega k\phi_A(2\langle n\rangle + 1) - \frac{k'}{\Omega}(4\langle n^3\rangle - 8\langle n^2\rangle + 4\langle n\rangle) \tag{5.4}$$

Performing the Gaussian approximation, we get:

$$\frac{d\langle n(t)\rangle}{dt} = \Omega k\phi_A + 2k'\frac{\langle n\rangle}{\Omega} - 2k'\frac{\langle n^2\rangle}{\Omega} \tag{5.5}$$

$$\frac{d\langle n^2(t)\rangle}{dt} = \Omega k\phi_A(2\langle n\rangle + 1) - \frac{k'}{\Omega}(12\langle n^2\rangle\langle n\rangle - 8\langle n\rangle^3 - 8\langle n^2\rangle + 4\langle n\rangle) \tag{5.6}$$

While first order van Kampen's expansion approach leads to:

$$\frac{d\phi}{dt} = k\phi A - 2k'\phi^2 \to \phi(t) = \frac{e^{2t}(\phi_0+1)+\phi_0-1}{e^{2t}(\phi_0+1)+1-\phi_0} \tag{5.7}$$

$$\begin{aligned} \frac{d\langle n\rangle}{dt} &= \Omega(k\phi_A + 2k'\phi^2) - 4k'\phi\langle n\rangle \\ \to \langle n(t)\rangle &= \frac{2[\langle n\rangle_0 - \Omega\phi_0 + \Omega\phi_0\cosh(2t)] + (1+\phi_0^2)\Omega\sinh(2t)}{2[\cosh(t)+\phi_0\sinh(t)]^2} \end{aligned} \tag{5.8}$$

$$\begin{aligned} \frac{d\langle n^2\rangle}{dt} &= -8k'\phi\langle n^2\rangle + \Omega(2k\phi_A + 4k'\phi^2)\langle n\rangle + \Omega(k\phi_A + 4k'\phi^2) \\ \to \langle n^2(t)\rangle &= \frac{e^{-4t}\Omega(\phi_0-1)^4(4\Omega-3) + e^{4t}\Omega(1+\phi_0)^4(3+4\Omega) + 64\langle n^2\rangle_0 - 8\Omega^2 + 8\Omega t}{64[\cosh(t)+\phi_0\sinh(t)]^4} \\ &+ \frac{8e^{-2t}\Omega(\phi_0-1)^2(\phi_0 - 1 - 4\langle n\rangle_0 + 4\Omega\phi_0) - 8e^{2t}\Omega(1+\phi_0)^2(-1-4\langle n\rangle_0 + 4\Omega\phi_0)}{64[\cosh(t)+\phi_0\sinh(t)]^4} \\ &+ \frac{8\Omega\phi_0(-7 - 16\langle n\rangle_0 + \phi_0(\phi_0 + 100 - 2t + \phi_0^2(t-\Omega) - e^{2t}\phi_0(1+\phi_0)^2))}{64[\cosh(t)+\phi_0\sinh(t)]^4} \end{aligned} \tag{5.9}$$

(The expressions given for $\phi(t)$, $\langle n(t)\rangle$ and $\langle n^2(t)\rangle$ correspond to the case $k\phi_A = 1$, $k' = 1/2$).

To compare the two approximations in the time-dependent case, we simulate the process using the Gillespie method. The Gillespie method allows us to obtain single realizations of the process, so to obtain the evolution of the moments we average over many (over one million) realizations.
In the next figures we show the results obtained with the Gaussian approximation (computed by numerical integration of equations 5.5, 5.6), van Kampen's expansion (equations 5.8, 5.9) and the Gillespie method, and the exact stationary solution obtained from (5.2), for different system sizes and initial conditions.

We see that the Gaussian approximation fits better the evolution of the mean value, but the variance is better approximated by the first order van Kampen's expansion. Again, the difference between the methods decreases as the system size is increased.
In figure (5.5) we show the error in $\langle n\rangle$ and $\langle n^2\rangle$ in the stationary state for the two approximations as a function of system size Ω. We see that the error in $\langle n\rangle$ decays as Ω^{-1} for the Gaussian approximation whereas the other errors scale as Ω^0, consistently with the analysis of the approximations performed.

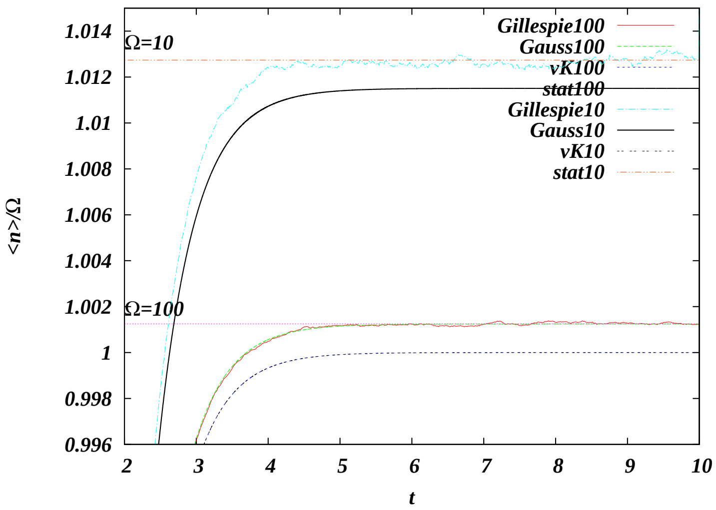

Figure 5.1. $\langle n(t)\rangle/\Omega$ for $k\phi_A = 1$, $k' = 1/2$, $n_0 = 0, \Omega = 10, 100$.
Gaussian approximation (green) is almost indistinguishable from Gillespie method (red) and exact result in the stationary case (pink) for $\Omega = 100$, whereas van Kampen's expansion result (dotted blue) is clearly different. For $\Omega = 10$ Gaussian approximation (black) is again closer to the Gillespie method (light blue) and exact stationary result (dashed orange) than van Kampen's expansion method (dashed black, independent of Ω) which is significantly far from the exact result.

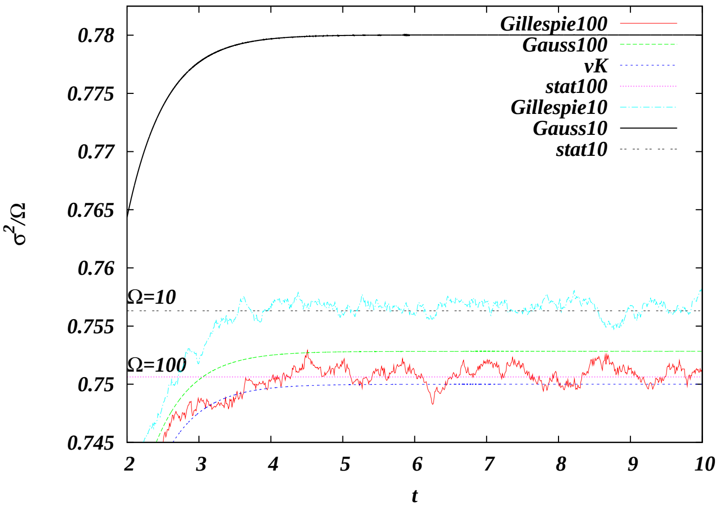

Figure 5.2. $\sigma^2(t)/\Omega$ for $k\phi_A = 1$, $k' = 1/2$, $n_0 = 0, \Omega = 10, 100$.
For $\Omega = 100$, van Kampen's expansion (dotted blue) reproduces slightly better the exact stationary value (pink) and Gillespie results (red) than Gaussian approximation (green). For $\Omega = 10$ van Kampen's expansion (independent of Ω) is significantly closer to Gillespie result (light blue) and exact stationary value (dashed black) than Gaussian approximation (black).

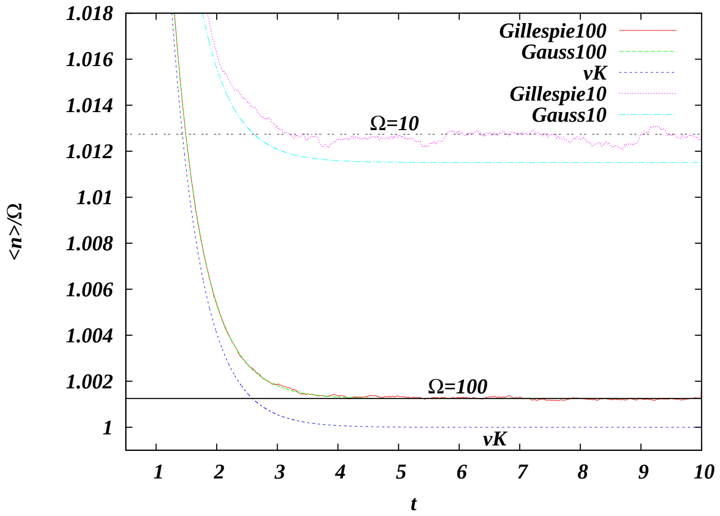

Figure 5.3. $\langle n(t)\rangle/\Omega$ for $k\phi_A = 1$, $k' = 1/2$, $n_0 = 1.05\Omega, \Omega = 10, 100$.
Gaussian approximation (green) is almost indistinguishable from Gillespie method (red) and exact result in the stationary case (black) for $\Omega = 100$, whereas van Kampen's expansion result (dotted blue) is clearly different. For $\Omega = 10$ Gaussian approximation (light blue) is again closer to the Gillespie method (pink) and exact stationary value (dashed black) than van Kampen's expansion method (dotted blue, independent of Ω) which is significantly far from the exact result.

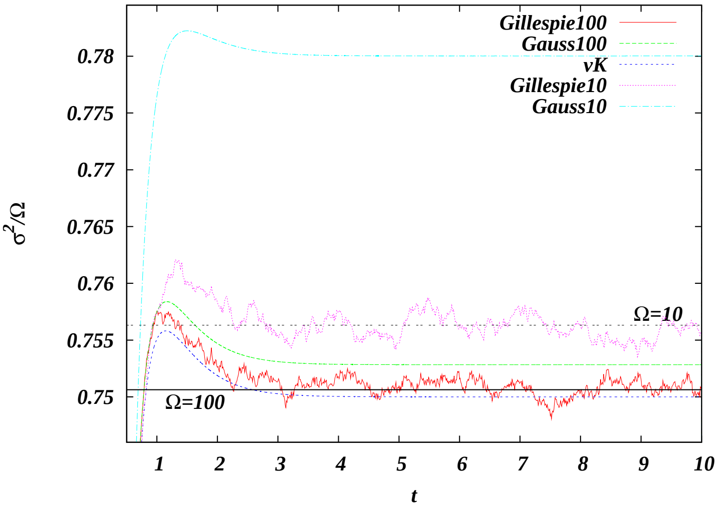

Figure 5.4. $\sigma^2(t)/\Omega$ for $k\phi_A = 1$, $k' = 1/2$, $n_0 = 1.05\Omega, \Omega = 10, 100$.
For $\Omega = 100$, van Kampen's expansion (dotted blue) reproduces better the exact stationary value (black) than Gaussian approximation (green). For $\Omega = 10$ van Kampen's expansion (independent of Ω) is significantly closer to the exact stationary value (dashed black) than Gaussian approximation (light blue).

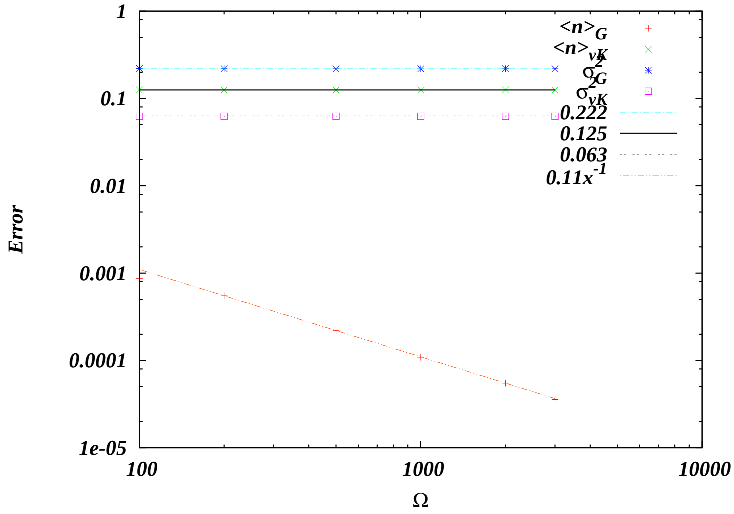

Figure 5.5. Error in $\langle n \rangle$ and σ^2 in the stationary case as a function of Ω for $k\phi_A = 1$, $k' = 1/2$.
For the Gaussian approximation, the error in $\langle n \rangle$ (red crosses) decays as Ω^{-1} while the error in σ^2 (blue stars) is constant with Ω. For van Kampen's expansion, both the error in $\langle n \rangle$ and in σ^2 are constant with Ω.

6

Opinion formation

In the last few years there has been a growing interest in the application of methods and techniques coming from statistical physics to the study of complex phenomena in fields traditionally farm from physics research such as biology, medicine, information technology or social systems. In particular the application of the physical approach to social phenomena has been discussed in several reviews [6].

In a recent paper [7] the opinion formation is modeled as follows:

We consider two parties, A and B, and an "intermediate" group of undecided agents I. The supporters of A and B do not interact among them, but only through their interaction with the group I, convincing one of its members with a given probability. In addition there is a nonzero probability of a spontaneous change of opinion from I to the other two parties and viceversa.

More specifically, if $N_{A(B)}$ is the number of supporters of party A(B), N_I is the number of undecided agents and N is the total number of individuals, the possible transitions are:

spontaneous change $A \rightarrow I$, occurring with a rate $\alpha_1 N_A$

spontaneous change $I \rightarrow A$, occurring with a rate $\alpha_2 N_I$

spontaneous change $B \rightarrow I$, occurring with a rate $\alpha_3 N_B$

spontaneous change $I \rightarrow B$, occurring with a rate $\alpha_4 N_I$

convincing rule $A + I \rightarrow 2A$, occurring with a rate $\frac{\beta_1}{N} N_A N_I$

convincing rule $B + I \rightarrow 2B$, occurring with a rate $\frac{\beta_2}{N} N_B N_I$

As the total number of individuals ($N = N_A + N_B + N_I$) is fixed, there are only two independent variables (we choose N_A and N_B so $N_I = N - N_A - N_B$) and the master equation of the process is:

$$
\begin{aligned}
&\frac{\partial}{\partial t}P(N_A,N_B,t)=\alpha_1(N_A+1)P(N_A+1,N_B,t)+\alpha_3(N_B+1)P(N_A,N_B+1,t)\\
&+\alpha_2(N-N_A-N_B+1)P(N_A-1,N_B,t)+\alpha_4(N-N_A-N_B+1)P(N_A,N_B-1,t)\\
&+(N-N_A-N_B+1)\left[\frac{\beta_1}{N}(N_A-1)P(N_A-1,N_B,t)+\frac{\beta_2}{N}(N_B-1)P(N_A,N_B-1,t)\right]\\
&-\left[\alpha_1N_A+\alpha_3N_B+(\alpha_2+\alpha_4)(N-N_A-N_B)+\tfrac{\beta_1N_A+\beta_2N_B}{N}(N-N_A-N_B)\right]P(N_A,N_B,t)
\end{aligned}
\tag{6.1}
$$

In this case N plays the role of the large parameter Ω. Again, we note that this master equation can be written in the general form (3.8) by setting $G_{1,0}=\alpha_1N_A$, $G_{0,1}=\alpha_3N_B$, $G_{-1,0}=(N-N_A-N_B)(\alpha_2+\frac{\beta_1}{N}N_A)$ and $G_{0,-1}=(N-N_A-N_B)(\alpha_4+\frac{\beta_2}{N}N_B)$.
There is not a known exact solution for this master equation so approximate methods to deal with it are needed.

The exact equations for the firsts moments are:

$$
\begin{aligned}
\frac{d\langle N_A(t)\rangle}{dt} &= -(\alpha_1+\alpha_2-\beta_1)\langle N_A\rangle+\alpha_2(N-\langle N_B\rangle)-\frac{\beta_1}{N}\langle N_A^2\rangle-\frac{\beta_1}{N}\langle N_AN_B\rangle \quad (6.2)\\
\frac{d\langle N_B(t)\rangle}{dt} &= -(\alpha_3+\alpha_4-\beta_2)\langle N_B\rangle+\alpha_4(N-\langle N_A\rangle)-\frac{\beta_2}{N}\langle N_B^2\rangle-\frac{\beta_2}{N}\langle N_AN_B\rangle \quad (6.3)\\
\frac{d\langle N_A^2(t)\rangle}{dt} &= (\alpha_1+\alpha_2(2N-1)+\beta_1)\langle N_A\rangle+\alpha_2(N-\langle N_B\rangle)-2(\alpha_1+\alpha_2-\beta_1+\frac{\beta_1}{2N})\langle N_A^2\rangle\\
&\quad -(2\alpha_2+\frac{\beta_1}{N})\langle N_AN_B\rangle-\frac{2\beta_1}{N}\langle N_A^3\rangle-\frac{2\beta_1}{N}\langle N_A^2N_B\rangle \quad (6.4)\\
\frac{d\langle N_B^2(t)\rangle}{dt} &= (\alpha_3+\alpha_4(2N-1)+\beta_2)\langle N_B\rangle+\alpha_4(N-\langle N_A\rangle)-2(\alpha_3+\alpha_4-\beta_2+\frac{\beta_2}{2N})\langle N_B^2\rangle\\
&\quad -(2\alpha_4+\frac{\beta_2}{N})\langle N_AN_B\rangle-\frac{2\beta_2}{N}\langle N_B^3\rangle-\frac{2\beta_2}{N}\langle N_AN_B^2\rangle \quad (6.5)\\
\frac{d\langle N_A(t)N_B(t)\rangle}{dt} &= -(\alpha_1+\alpha_2+\alpha_3+\alpha_4-\beta_1-\beta_2)\langle N_AN_B\rangle+\alpha_2(N\langle N_B\rangle-\langle N_B^2\rangle)\\
&\quad +\alpha_4(N\langle N_A\rangle-\langle N_A^2\rangle)-\frac{\beta_1+\beta_2}{N}(\langle N_A^2N_B\rangle+\langle N_AN_B^2\rangle) \quad (6.6)
\end{aligned}
$$

Performing the Gaussian approximation leads to:

$$\frac{d\langle N_A(t)\rangle}{dt}=-(\alpha_1+\alpha_2-\beta_1)\langle N_A\rangle+\alpha_2N-\alpha_2\langle N_B\rangle-\frac{\beta_1}{N}\langle N_A^2\rangle-\frac{\beta_1}{N}\langle N_AN_B\rangle \tag{6.7}$$

$$\frac{d\langle N_B(t)\rangle}{dt}=-(\alpha_3+\alpha_4-\beta_2)\langle N_B\rangle+\alpha_4N-\alpha_4\langle N_A\rangle-\frac{\beta_2}{N}\langle N_B^2\rangle-\frac{\beta_2}{N}\langle N_AN_B\rangle \tag{6.8}$$

$$
\begin{aligned}
\frac{d\langle N_A^2(t)\rangle}{dt} &= (\alpha_1+\alpha_2(2N-1)+\beta_1)\langle N_A\rangle+\alpha_2(N-\langle N_B\rangle)-2(\alpha_1+\alpha_2-\beta_1+\tfrac{\beta_1}{2N})\langle N_A^2\rangle\\
&\quad -(2\alpha_2+\tfrac{\beta_1}{N})\langle N_AN_B\rangle-\tfrac{2\beta_1}{N}(3\langle N_A\rangle\langle N_A^2\rangle-2\langle N_A\rangle^3)\\
&\quad -\tfrac{2\beta_1}{N}(\langle N_A^2\rangle\langle N_B\rangle+2\langle N_A\rangle\langle N_AN_B\rangle-2\langle N_A\rangle^2\langle N_B\rangle)\\
\frac{d\langle N_B^2(t)\rangle}{dt} &= (\alpha_3+\alpha_4(2N-1)+\beta_1)\langle N_B\rangle+\alpha_4(N-\langle N_A\rangle)-2(\alpha_3+\alpha_4-\beta_2+\tfrac{\beta_2}{2N})\langle N_B^2\rangle\\
&\quad -(2\alpha_4+\tfrac{\beta_2}{N})\langle N_AN_B\rangle-\tfrac{2\beta_2}{N}(3\langle N_B\rangle\langle N_B^2\rangle-2\langle N_B\rangle^3)\\
&\quad -\tfrac{2\beta_2}{N}(\langle N_B^2\rangle\langle N_A\rangle+2\langle N_B\rangle\langle N_AN_B\rangle-2\langle N_B\rangle^2\langle N_A\rangle)\\
\frac{d\langle N_A(t)N_B(t)\rangle}{dt} &= -(\alpha_1+\alpha_2+\alpha_3+\alpha_4-\beta_1-\beta_2)\langle N_AN_B\rangle+\alpha_2(N\langle N_B\rangle-\langle N_B^2\rangle)\\
&\quad +\alpha_4(N\langle N_A\rangle-\langle N_A^2\rangle)-\tfrac{\beta_1+\beta_2}{N}(\langle N_A^2N_B\rangle+\langle N_AN_B^2\rangle)
\end{aligned}
$$

In van Kampen's expansion method, we define $\phi_{A(B)},\xi_{A(B)}$ such that

$$N_{A(B)}=N\phi_{A(B)}+N^{1/2}\xi_{A(B)} \tag{6.9}$$

The equations for the macroscopic components are ([7]):

$$\frac{d\phi_A}{dt}=-\alpha_1\phi_A+[\alpha_2+\beta_1\phi_A](1-\phi_A-\phi_B) \tag{6.10}$$

$$\frac{d\phi_B}{dt}=-\alpha_3\phi_B+[\alpha_4+\beta_2\phi_B](1-\phi_A-\phi_B) \tag{6.11}$$

And for the fluctuations:

$$\frac{d\langle\xi_A\rangle}{dt} = -[\alpha_1+\alpha_2+\beta_1(2\phi_A+\phi_B)-\beta_1]\langle\xi_A\rangle-(\alpha_2+\beta_1\phi_A)\langle\xi_B\rangle \tag{6.12}$$

$$\frac{d\langle\xi_B\rangle}{dt} = -[\alpha_3+\alpha_4+\beta_2(2\phi_B+\phi_A)-\beta_2]\langle\xi_B\rangle-(\alpha_4+\beta_2\phi_B)\langle\xi_A\rangle \tag{6.13}$$

$$
\begin{aligned}
\frac{d\langle\xi_A^2\rangle}{dt} &= -2\alpha_1\langle\xi_A^2\rangle-2(\alpha_2+\beta_1\phi_A)(\langle\xi_A^2\rangle+\langle\xi_A\xi_B\rangle)+2\beta_1\langle\xi_A^2\rangle(1-\phi_A-\phi_B)\\
&\quad +\alpha_1\phi_A+(\alpha_2+\beta_1\phi_A)(1-\phi_A-\phi_B)
\end{aligned} \tag{6.14}
$$

$$
\begin{aligned}
\frac{d\langle\xi_B^2\rangle}{dt} &= -2\alpha_3\langle\xi_B^2\rangle-2(\alpha_4+\beta_2\phi_B)(\langle\xi_B^2\rangle+\langle\xi_A\xi_B\rangle)+2\beta_2\langle\xi_B^2\rangle(1-\phi_A-\phi_B)\\
&\quad +\alpha_3\phi_B+(\alpha_4+\beta_2\phi_B)(1-\phi_A-\phi_B)
\end{aligned} \tag{6.15}
$$

$$
\begin{aligned}
\frac{d\langle\xi_A\xi_B\rangle}{dt} &= -(\alpha_1+\alpha_3)\langle\xi_A\xi_B\rangle-(\alpha_2+\beta_1\phi_A)(\langle\xi_A\xi_B\rangle+\langle\xi_B^2\rangle)-(\alpha_4+\beta_2\phi_B)(\langle\xi_A\xi_B\rangle+\langle\xi_A^2\rangle)\\
&\quad +(1-\phi_A-\phi_B)(\beta_1+\beta_2)\langle\xi_A\xi_B\rangle
\end{aligned} \tag{6.16}
$$

From those we can recover the expression in the original variables through (6.9).

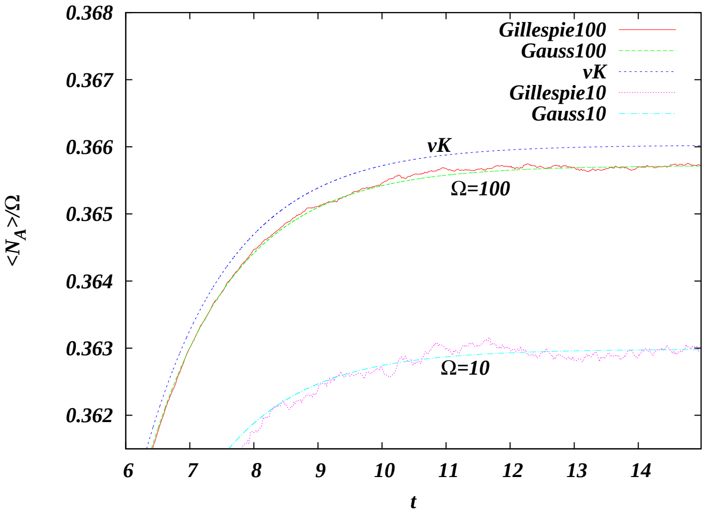

Figure 6.1. $\langle N_A(t)\rangle/\Omega$ for $N_{A,0} = 0, N_{B,0} = \Omega, \Omega = 10, 100$ and $\alpha_i = \beta_i = 1$. Gaussian approximation (green and light blue) follows precisely the Gillespie result whereas van Kampen's expansion (doted blue, independent of Ω) differs clearly, specially for $\Omega = 10$.

In the next figures we compare the results coming from both approximations (obtained by numerical integration of the previous equations) and from simulations of the process performed with the Gillespie algorithm, for different sistem sizes and some representative values of the parameters and initial conditions.

Again, the Gaussian approximation reproduces better the values for the average whereas in this case both methods are very similar for the fluctuations and correlation.

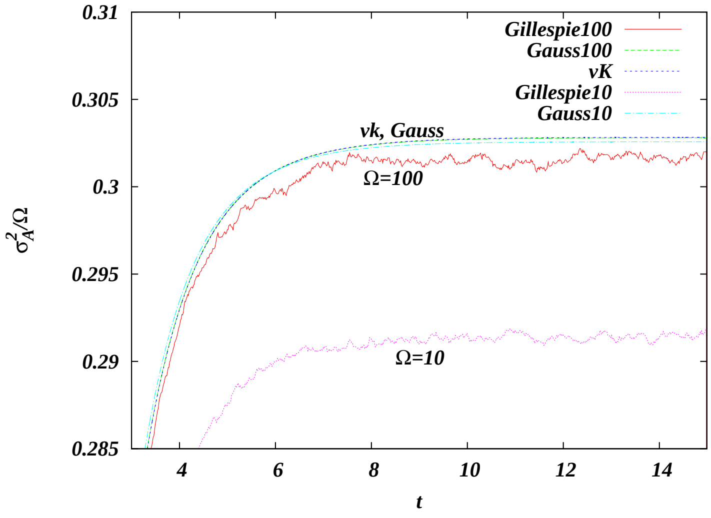

Figure 6.2. $\sigma_A^2(t)/\Omega$ for $N_{A,0} = 0, N_{B,0} = \Omega, \Omega = 10, 100$ and $\alpha_i = \beta_i = 1$.
Gaussian approximation results (green and light blue) are almost independent of system size and very close to van Kampen's expansion results (dotted blue). Both are close to the Gillespie results for $\Omega = 100$, but differ clearly from those for $\Omega = 10$.

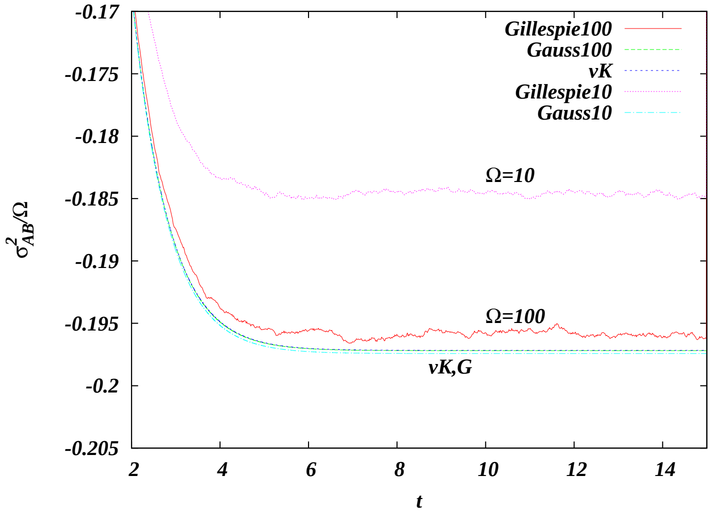

Figure 6.3. $\sigma_{AB}^2(t)/\Omega$ for $N_{A,0} = 0, N_{B,0} = \Omega, \Omega = 10, 100$ and $\alpha_i = \beta_i = 1$.
Again Gaussian approximation is very close to van Kampen's expansion and both methods fail for small Ω.

7

Conclusions

In summary, we have proposed a method to obtain the average and variance of a stochastic process that follows a master equation.

The method is based on assuming that the probability distribution is Gaussian and using this knowledge to express higher order moments as a function of the two firsts in the exact equations for these. Although this hypothesis is derived in van Kampen's approach, our method is not fully equivalent to it.

We have shown that, for a general class of master equations, the Gaussian approximation leads to an error in the mean value that scales as one over the square root of the system size and an error in the variance that scales as the square root of the system size. In this respect is better than first order van Kampen's expansion (error in mean value $\sim O(\Omega^0)$, error in $\sigma^2 \sim O(\Omega^{1/2})$). Besides that, another advantage of the method is its simplicity and easy implementation.

In all the examples where we have applied the method it performs better than first order van Kampen's expansion for the mean value. For the variance it results better in the reaction-limited process, worse in the autocatalitic reaction and almost equal for the opinion formation model.

Taking into account it's simplicity, we believe that this method can be used as an alternative to van Kampen's expansion when there is no intention of going further than first order.

Bibliography

[1] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 2004).

[2] C. W Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences* (Springer-Verlag, 1990).

[3] W. Feller, *An introduction do Probabibility Theory and its Applications*, Vol. I(Wiley, New York 1966).

[4] I.I.Gihman and A.V.Skorohod *The theory of Stochastic Processes I* (Springer-Verlag, Berlin Heidelberg New York 1974).

[5] D. T. Gillespie. J. Phys. Chem. **81**,2340-2361 (1977).

[6] W. Weidlich, *Sociodynamics- A systematic approach to mathematical modelling in social sciences* (Taylor and Francis, London, 2002). W Weidlich Phys. Rep. **204**, 1 (1991). D. Stauffer, S. Moss de Oliveira, P.M.C. de Oliveira, J.S. Sa Martins, *Biology, Sociology, Geology by Computational Physicists* (Elsevier, Amsterdam, 2006). Castellano, C., Fortunato, S., Loreto, V. Rev. Mod. Phys. **81**,591-646 (2009).

[7] M. S. de la Lama, I.G. Szendro, J.R. Iglesias, H.S. Wio, Eur. Phys. J. B **51**, 435-442 (2006).

8

Appendix 1: Reaction-limited process

8.1 Introduction

Consider the general process $A+B \underset{\omega}{\overset{\kappa}{\rightleftharpoons}} C$, limited by reaction. This means that any two particles A and B have the same probability of reaction. Denoting by $A(t)$ and $B(t)$, respectively, the number of particles of the A and B substances, the rate for the $A+B \longrightarrow C$ reaction is $\frac{\kappa}{\Omega}A(t)B(t)$. For the reverse reaction, it is assumed that C has a constant concentration, and hence the rate is $\omega\Omega$. In these expressions Ω is proportional to the total volume accessible to particles. Since $B(t)-A(t) \equiv \Delta$ is a constant, one only needs to consider one variable, for example, the number of A particles at time t. Let us denote by $P_n(t)$ the probability that there are n A-particles at time t. The master equation describing the process is obtained from:

$$\begin{array}{rcl} P_n(t+dt) & = & P_{n+1}(t)\frac{\kappa}{\Omega}(n+1)(\Delta+n+1)dt+ \\ & & P_{n-1}(t)\omega\Omega dt + P_n(t)[1-\frac{k}{\Omega}n(\Delta+n)dt][1-\omega\Omega dt] \end{array} \tag{8.1}$$

or

$$\frac{dP_n(t)}{dt} = \frac{\kappa}{\Omega}\left[(n+1)(\Delta+n+1)P_{n+1}(t) - n(n+\Delta)P_n(t)\right] + \omega\Omega[P_{n-1}(t)-P_n(t)] \tag{8.2}$$

which is the basis of the subsequent analysis.

By defining the moments $\langle n(t)^k\rangle = \sum_n n^k P_n(t)$, it is simple to arrive at:

$$\frac{d\langle n(t)\rangle}{dt} = -\frac{\kappa}{\Omega}\left(\langle n(t)^2\rangle + \Delta\langle n(t)\rangle\right) + \omega\Omega \tag{8.3}$$

The typical mean-field assumption neglects fluctuations and approximates $\langle n(t)^2\rangle \approx \langle n(t)\rangle^2$. By defining the density of particles $\rho(t) = \dfrac{\langle n(t)\rangle}{\Omega}$ one obtains

$$\frac{d\rho(t)}{dt} = -\kappa\rho(t)(\rho(t)+\delta) + \omega \tag{8.4}$$

with $\delta = \Delta/\Omega$. The solution of this differential equation with the initial condition $\rho(t=0) = \rho_0$ is:

$$\rho(t) = \frac{\rho_1 - \rho_2 \tilde{\rho} \mathrm{e}^{-\lambda t}}{1 - \tilde{\rho} \mathrm{e}^{-\lambda t}} \tag{8.5}$$

with $\rho_{1,2} = -\frac{\delta}{2} \pm \sqrt{\frac{\delta^2}{4} + \frac{\omega}{\kappa}}$, $\tilde{\rho} = \frac{\rho_0 - \rho_1}{\rho_0 - \rho_2}$ and $\lambda = \kappa\sqrt{\delta^2 + 4\omega/\kappa}$. As $t \to \infty$ the concentration of A particles tends to the equilibrium value ρ_1 exponentially:

$$\rho(t) - \rho_1 \approx (\rho_1 - \rho_2)\tilde{\rho}\mathrm{e}^{-\lambda t} \tag{8.6}$$

An exception to this exponential decay occurs in the irreversible, $\omega = 0$, and symmetric, $\delta = 0$, case. In this case, $\rho_1 = \rho_2 = \lambda = 0$ and the solution can be obtained as the suitable limit of Eq.(8.5) or, more easily, starting from Eq.(8.4) with $\delta = \omega = 0$:

$$\rho(t) = \frac{\rho_0}{1 + \rho_0 \kappa t} \tag{8.7}$$

i.e. a potential t^{-1} decay towards equilibrium.

This mean-field treatment neglects fluctuations. The purpose of these notes is to find the exact solution of the master equation (8.2) and to obtain the correct asymptotic time dependence for the average number of particles $\langle n(t) \rangle$ and the fluctuations $\langle n(t)^2 \rangle - \langle n(t) \rangle^2$.

8.2 Solution of the master equation

Without loss of generality, let us rescale $t \to \kappa t/\Omega$ and $\omega \to \omega\Omega^2/\kappa$ to get the simpler equation:

$$\frac{dP_n(t)}{dt} = (n+1)(\Delta + n + 1)P_{n+1}(t) - n(n+\Delta)P_n(t) + \omega[P_{n-1}(t) - P_n(t)] \tag{8.8}$$

Furthermore, only the case $\Delta \geq 0$ needs to be considered. If $\Delta < 0$ the change $m = n - \Delta$ leaves invariant the previous equation provided that we make the identification $P_n(t) \to P_{n+\Delta}(t)$. This means that the solutions in both cases are related by $P_n(t;\Delta) = P_{n-\Delta}(t;-\Delta)$.

Introducing the generating function

$$f(s,t) = \sum_{n=0}^{\infty} P_n(t) s^n, \tag{8.9}$$

one arrives at the partial differential equation:

$$\frac{\partial f}{\partial t} = (1-s)\left[s\frac{\partial^2 f}{\partial s^2} + (1+\Delta)\frac{\partial f}{\partial s} - \omega f\right] \tag{8.10}$$

It is possible to obtain the general solution of this equation in the irreversible case $\omega = 0$. This solution will be presented later. We first discuss the equilibrium solution in the general case.

8.2.1 The equilibrium solution

By setting $\frac{\partial f}{\partial t} = 0$ one gets the differential equation:

$$s\frac{\partial^2 f}{\partial s^2} + (1+\Delta)\frac{\partial f}{\partial s} - \omega f = 0 \tag{8.11}$$

The solution around the singular regular point $s = 0$ can be found by the Frobenius method as a power series $\sum_{n=0}^{\infty} a_n s^{n+\nu}$. The regular solution satisfying the boundary condition $f(s=1) = 1$ is[1]:

$$f(s) = \frac{s^{-\Delta/2} I_\Delta\left(2\sqrt{\omega s}\right)}{I_\Delta\left(2\sqrt{\omega s}\right)} \tag{8.12}$$

and the equilibrium probabilities are:

$$P_n = \frac{\omega^{n+\Delta/2}}{I_\Delta\left(2\sqrt{\omega}\right) n!(n+\Delta)!} \tag{8.13}$$

from where the first two moments can be computed as:

$$\langle n \rangle = \frac{I_{\Delta+1}\left(2\sqrt{\omega}\right)}{I_\Delta\left(2\sqrt{\omega}\right)}\sqrt{\omega} \tag{8.14}$$

$$\langle n^2 \rangle = \omega - \frac{I_{\Delta+1}\left(2\sqrt{\omega}\right)}{I_\Delta\left(2\sqrt{\omega}\right)}\Delta\sqrt{\omega} \tag{8.15}$$

8.2.2 The time-dependent solution

We now study how the system relaxes towards equilibrium. We will restrict ourselves to the irreversible case $\omega = 0$. This corresponds to the process $A + B \rightarrow 0$, inert. This is the case considered in the main text. The partial differential equation (8.10) can be solved by the technique of separation of variables by trying solutions of the form $f(s,t) = f_1(s) f_2(t)$. This leads to the pair of ordinary differential equations:

$$s(1-s)f_1'' + (1-s)(1+\Delta)f_1' + \lambda^2 f_1 = 0 \tag{8.16}$$

$$f_2' + \lambda^2 f_2 = 0 \tag{8.17}$$

being λ^2 the constant arising from the method of separation of variables. The solution of the time dependent function is $\mathrm{e}^{-\lambda^2 t}$ and the solution of the s-function is the hypergeometric function[2] $F(-\mu_1, \mu_2; \Delta+1; s)$. The explicit series is:

$$F(-\mu_1, \mu_2; \Delta+1; s) = \sum_{n=0}^{\infty} \frac{(-\mu_1)_n (\mu_2)_n}{(\Delta+1)_n} \frac{s^n}{n!} \tag{8.18}$$

---

[1] There is another solution to this equation, but it contains a term in $\ln s$ and it has to be discarded since it can not be expanded in a power series of s. In the following $I_n(z)$ is the modified Bessel function of the first kind.

[2] There is another solution to the second-order differential equation. As before, this solution has to be discarded since it can not be expanded in powers of s.

$(a)_n$ is the Pochhammer's symbol: $(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)}$, or $(a)_0 = 1$, $(a)_n = a(a+1)\dots(a+n-1)$ for $n > 0$, and we have introduced

$$\mu_1 = \frac{-\Delta + \sqrt{\Delta^2 + 4\lambda^2}}{2} \tag{8.19}$$

$$\mu_2 = \frac{\Delta + \sqrt{\Delta^2 + 4\lambda^2}}{2} \tag{8.20}$$

The solution for the function $f(s,t)$ is obtained by linear combination of the elementary solutions found above:

$$f(s,t) = \sum_\lambda C_\lambda F(-\mu_1, \mu_2; \Delta + 1; s)\mathrm{e}^{-\lambda^2 t} \tag{8.21}$$

This function is, in general, an infinite series on the variable s. In fact the coefficients, according to (8.9) are nothing but the time-dependent probabilities. However, in this irreversible case, the probability of having more A-particles that the initial number at $t = 0$, say M, has to be zero. Therefore the series must be truncated after the power s^M. This implies that in the previous expression only hypergeometric functions that represent a polynomial in s can be accepted. This is achieved by forcing $\mu_1 = k = 0, 1, 2 \dots, M$, since the series (8.18) becomes then a polynomial of degree k. The condition $\mu_1 = k$ is equivalent to the parameter λ adopting one of the possible values $\lambda_k = \sqrt{k(k + \Delta)}$. Finally, noticing that $\mu_2 - \mu_1 = \Delta$, the solution can be written as:

$$f(s,t) = \sum_{k=0}^{M} \sum_{n=0}^{k} C_k(\Delta, M)\mathrm{e}^{-k(k+\Delta)t} B_{n,k}(\Delta) s^n \tag{8.22}$$

The notation emphasizes that C_k depends both on Δ and M but $B_{n,k}$ depends only on Δ:

$$B_{n,k}(\Delta) = \frac{(-k)_n (k + \Delta)_n}{n!(\Delta + 1)_n} \tag{8.23}$$

All that remains is to impose the initial condition. We start with M A-particles at time $t = 0$, such that $f(s, t = 0) = s^M$. This implies that the coefficients C_k must satisfy:

$$\sum_{k=n}^{M} B_{n,k} C_k = \delta_{n,M} \tag{8.24}$$

for $n = 0, 1, \dots, M$. The solution starts by finding first $C_M = 1/B_{M,M}$ and then proceeds backwards to find $C_{M-1}, C_{M-2}, \dots, C_0$ in a recursive manner. After some lengthy algebra, the result is:

$$C_k(\Delta, M) = (-1)^k \frac{2k + \Delta}{k + \Delta} \frac{(k+1)_\Delta}{\Delta!} \frac{(M - k + 1)_k}{(M + \Delta + 1)_k} \tag{8.25}$$

(in the case $\Delta = k = 0$ the correct interpretation of the undetermined expression is $C_0 = 1$). We now give the expression for the probabilities:

$$P_n(t) = \sum_{k=n}^{M} C_k(\Delta, M) B_{n,k}(\Delta)\mathrm{e}^{-k(k+\Delta)t} \tag{8.26}$$

Figure 8.1. Equilibrium values $\langle n\rangle/\Omega$ and normalized fluctuations $\Omega^{-1}\sqrt{\langle n^2\rangle - \langle n\rangle^2}$ versus volume Ω for $\kappa = 1$, $\omega = 1$, $\delta = 1$. The mean value tends to the infinite volume result, $0.618\ldots$, while fluctuations decrease as $\frac{2}{3}\Omega^{-1/2}$.

The normalization condition $\sum_{n=0}^{M} P_n(t) = 1$ is verified with the help of the relation $\sum_{n=0}^{k} B_{n,k} = \delta_{k,0}$. The relation $\displaystyle\sum_{n=0}^{k} nB_{n,k} = (-1)^k k\frac{\Delta!}{(k)_\Delta}$ (the indetermination arising when $\Delta = k = 0$ must be resolved as 0) helps to find the average of the number of particles:

$$\langle n(t)\rangle = \sum_{k=1}^{M}(2k+\Delta)\frac{(M-k+1)_k}{(M+\Delta+1)_k}\mathrm{e}^{-k(k+\Delta)t} \tag{8.27}$$

The second moment $\langle n(t)^2\rangle$ can be found with the help of Eq.(8.3) (remember that the time has been rescaled) as $\langle n(t)^2\rangle = -\dfrac{d\langle n(t)\rangle}{dt} - \Delta\langle n(t)\rangle$, or:

$$\langle n(t)^2\rangle = \sum_{k=1}^{M}(2k+\Delta)(k^2+(k-1)\Delta)\frac{(M-k+1)_k}{(M+\Delta+1)_k}\mathrm{e}^{-k(k+\Delta)t} \tag{8.28}$$

8.3 Comparison with the mean-field solution

In the limit $\Omega \to \infty$ the fluctuations should be negligible and the mean-field result should be recovered.

8.3.1 The equilibrium case

The limit is somewhat complicated from the technical point of view[3] but it can be checked that indeed Eq.(8.14) (after restoring $\omega \to \omega\Omega^2/\kappa$) gives that the equilibrium concentration $\rho = \frac{\langle n\rangle}{\Omega}$ tends to ρ_1, the mean field equilibrium value, when $\Omega \to \infty$, keeping $\delta = \Delta/\Omega$ finite. It can also be checked that in the same limit, the normalized fluctuations $\sigma[n]/\Omega$, with $\sigma^2[n] = \langle n^2\rangle - \langle n\rangle^2$, are of order $\Omega^{-1/2}$ and vanish in the large volume limit.

8.3.2 The time-dependent case

In the limit $t \to \infty$ the leading expression for $\langle n(t)\rangle$ corresponds to the term $k = 1$ in the sum of Eq.(8.27). Introducing back the original time scale, we get in this limit:

$$\langle n(t)\rangle \sim \frac{(2+\Delta)M}{M+\Delta+1}\mathrm{e}^{-(1+\Delta)\kappa t/\Omega} \tag{8.29}$$

Recalling that $\rho(t) = \langle n(t)\rangle/\Omega$, $\delta = \Delta/\Omega$ and $\rho_0 = M/\Omega$, we get in the limit of large Ω:

$$\rho(t) \sim \frac{\rho_0\delta}{\delta+\rho_0}\mathrm{e}^{-\delta\kappa t} \tag{8.30}$$

which coincides with Eq.(8.6) (with $\omega = 0$) in this large Ω and large t limit.

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[3] The expansion 9.7.7 in Abramowitz and Stegun is useful.

The case $\Delta = 0$ is more complicated. If we just take the leading order term in Eq.(8.27), we arrive at:

$$\rho(t) \sim \frac{2}{\Omega} \mathrm{e}^{-\kappa t/\Omega} \tag{8.31}$$

which says that $\rho(t) \sim 0$ decays exponentially, contrary to the mean-field result. To get a better understanding of what is happening we use the following approximation:

$$\ln \frac{(M-k+1)_k}{(M+1)_k} = \sum_{i=1}^{k} \ln \left(1 - \frac{k}{M+i}\right) \approx \sum_{i=1}^{k} \frac{-k}{M} = -\frac{k^2}{M} \tag{8.32}$$

valid in the limit of $M \to \infty$, and then replace the sum in (8.27) by an integral:

$$\langle n(t) \rangle = \int_{k=0}^{\infty} dk 2k \mathrm{e}^{-\left(\frac{1}{M} + \frac{\kappa t}{\Omega}\right) k^2} = \frac{M}{1 + \frac{M}{\Omega} \kappa t} \tag{8.33}$$

which is equivalent to Eq.(8.7). This potential decay is observed up to times of order $t \sim \Omega$ where there is a transition to the exponential decay (8.31). Therefore, the mean-field result is valid up to times of order Ω.

9

Appendix2: Autocatalitic reaction

In this case, the probability generanting function obeys the following partial differential equation:

$$\frac{\partial G(s,t)}{\partial t} = (1-s)\left[-k\Omega\phi_A G(s,t) + \frac{k'}{\Omega}(1+s)\frac{\partial^2 G(s,t)}{\partial s^2}\right] \tag{9.1}$$

It's general solution is not known. Howhever, the stady state solution follows:

$$(1+s)\frac{\partial^2 G(s)}{\partial s^2} = k\Omega\phi_A G(s) + \frac{k'}{\Omega} \tag{9.2}$$

Making the change of variables $1+s=x$, and setting $b \equiv \frac{k\phi_A}{k'}\Omega^2$, we obtain:

$$x\frac{d^2 G(x)}{dx^2} = bG \tag{9.3}$$

This is the Bessel equation and it's solution is given by:

$$G(s) = \sqrt{b(1+s)}\left[C_1 I_1(2\sqrt{b(1+s)}) + C_2 K_1(2\sqrt{b(1+s)})\right] \tag{9.4}$$

Where $I_1(z)$, $K_1(z)$ are the modified Bessel functions of first and second kind. The series expanssion of I_1, $I_1(z) = \sum a_n z^n$, has $a_n > 0$, whereas in the one of K_1, $K_1(z) = \sum b_n z^n$, b_n has no definite sign. As the series expanssion of $G(s)$, $G(s) = \sum P(n)s^n$, has $P(n) > 0$, we choose $C_2 = 0$. The normalicing condition $G(1) = 1$ leads to:

$$G(s) = \sqrt{\frac{1+s}{2}}\frac{I_1(2\sqrt{b(1+s)})}{I_1(2\sqrt{2b})} \tag{9.5}$$

To find $P^{st}(n)$ we need to expand G in powers of s. Taking into account that:

$$I_v(x) = \sum_{m=0}^{\infty}\frac{1}{m!(m+v)!}(\frac{x}{2})^{2m+v} \tag{9.6}$$

We have:

$$G(s) = \frac{1}{\sqrt{2}I_1(2\sqrt{2b})}\sum_{m=0}^{\infty}\frac{b^{m+1/2}}{m!(m+1)!}(1+s)^{m+1} = \frac{1}{\sqrt{2}I_1(2\sqrt{2b})}\sum_{m=0}^{\infty}\frac{b^{m+1/2}}{m!(m+1)!}\sum_{k=0}^{m+1}\frac{(m+1)!}{k!(m+1-k)!}s^k \tag{9.7}$$

$\sum_{m=0}^{\infty}\sum_{k=0}^{m+1} = \sum_{k=0}^{\infty}\sum_{m=k-1}^{\infty}$ but m starting at 0 if k=0.

$$G(s) = \frac{1}{\sqrt{2}I_1(2\sqrt{2b})}\sum_{k=0}^{\infty}\frac{s^k}{k!}\sum_{n=0}^{\infty}\frac{b^{n+k-1/2}}{n!(n+k-1)!} \tag{9.8}$$

(n=m-k+1, n starting at 1 if k=0). As $b^{n+k-1/2} = b^{k/2}\left(\frac{2\sqrt{b}}{2}\right)^{2n+k-1}$, for $n \geq 1$ we have:

$$P^{st}(n) = \frac{b^{n/2}I_{n-1}(2\sqrt{b})}{\sqrt{2}I_1(2\sqrt{2b})n!} \tag{9.9}$$

For $n = 0$:

$$\frac{1}{\sqrt{2}I_1(2\sqrt{2b})}\sum_{k=1}^{\infty}\frac{\left(\frac{2\sqrt{b}}{2}\right)^{2k-1}}{k!(k-1)!} = \frac{1}{\sqrt{2}I_1(2\sqrt{2b})}\sum_{l=0}^{\infty}\frac{\left(\frac{2\sqrt{b}}{2}\right)^{2l+1}}{l!(l+1)!} = \frac{1}{\sqrt{2}I_1(2\sqrt{2b})}I_1(2\sqrt{b})$$

As $I_{-1}(x) = I_1(x)$, and $b = \frac{kn_A}{k'}\Omega$ we have the final result:

$$P^{st}(n) = \frac{(kn_A\Omega/k')^{n/2}I_{n-1}(2\sqrt{k\Omega n_A/k'})}{n!\sqrt{2}I_1(2\sqrt{2k\Omega n_A/k'})} \tag{9.10}$$

wich is the expression (5.2) of the main text.