Systematic method for solving transport equations derived from master equations

Otto J. Eder and Thomas Lackner
Austrian Research Center, Seibersdorf, A-2444 Seibersdorf, Austria
(Received 22 March 1983)

It is shown how a one-dimensional transport equation (derived from a master equation) for a time-dependent conditional average of an arbitrary function can be solved successively, if the moments of the transition probability can be expanded in a series of a special parameter. The transport equation for the time-dependent conditional average value can be transformed into a set of l linear partial differential equations of first order for the lth approximation of the conditional average value. The system of equations is closed in the sense that the lth partial differential equation is determined by the solutions of the $l-1$ partial differential equations. It is shown how the results obtained compare with the linear noise approximation. Two examples are chosen to illustrate the way to use the method. One is the classical example of the diffusion of a Brownian particle, the other is Alkemade's diode.

I. INTRODUCTION

When treating many-body systems a wide variety of problems can be formulated in terms of a master equation for a Markov process. Mathematically the starting point is the Chapman-Kolmogorov equation, which must be fulfilled for any Markov process. The term master equation is commonly reserved for an integro-differential equation for a distribution function of a random variable and describes the rate of change of a particular state in terms of time-independent transition probabilities. Master equations in the above sense have found wide applications in dealing with transport problems in physics, chemical reaction kinetics, population changes in biology, sociology, etc. The crucial quantity in a master equation is the transition probability from one state to another, where, e.g., physical intuition mixed with plausibility arguments to first principle calculations in quantum-statistical mechanics introduce the necessary complexity of the physics involved in an otherwise formally simple balance equation.

There are a few properties of the system and the transition probability which we tacitly assume in the following. We consider homogeneous Markov processes in one dimension with a state space which may be discrete or continous but must be unbounded. There are instantaneous transitions from one state to another in the sense that changes on the microscopic scale can be separated from the changes on the macroscopic scale which are described by the master equation. We assume a time-independent transition probability for which moments exist and for which a natural or an artificially introduced parameter Ω can be found which serves as an expansion parameter. There is no need for assuming microreversibility (detailed balance). Currently we are trying to extend the method to an n-dimensional vector space.

In a recent review article on stochastic processes Hänggi and Thomas[1] describe the modern development for discrete and continuous master equations in great detail giving extensive references. While for discrete processes there are several new methods in use,[2,3] the standard treatment for continuous processes is to transform the master equation into a nonlinear Fokker-Planck equation (where the nonlinearity makes a renormalization of the transport equation necessary[4–6]) or to use an eigenfunction expansion for the original master equation directly.

Van Kampen has provided a method[7,8] for calculating approximations to the time-dependent distribution function in a systematic way by expanding the transition probability in terms of a suitably chosen parameter Ω. In his linear noise approximation he arrives at a linear Fokker-Planck equation with time-dependent coefficients which are determined by the macroscopic law. Kubo *et al.*[9] have developed a method to calculate the characteristic function of the time-dependent distribution function, assuming an exponential form for this function and expanding the exponent in a power series of $1/\Omega$. A time-dependent distribution function derived in one of these ways can, of course, be used to calculate time-dependent averages of physical quantities of interest, but it seems more appropriate to calculate these quantities directly to a well-defined order of approximation, and we will show how this can be done. In return, a direct calculation of moments can be used to construct an approximate time-dependent distribution function or its equilibrium limit. Methods in use are, e.g., the Edgeworth series development (product of a Gaussian distribution and a polynomial) or the Pearson distribution. Both approaches can be used to fit a certain number of moments and have different merits. An advantage of our method is that one can keep trace of the terms which are neglected when calculating a time-dependent average of a physical quantity with the aid of a time-dependent Gaussian distribution function. As will become clear later on, in contrast to our method, van Kampen's method does not give a systematic expansion method for time-dependent average values of a physical quantity in the expansion parameters Ω, which seems to justify our method.

A few examples, where the time-dependent average values are of interest, are the calculation of transport coefficients, the statistical description of Alkemade's diode,[10,11] Brownian motion, energy loss of neutral atoms, ions or electrons in gases or plasmas, concentration changes in chemical reactions, implantation profile computations, etc.

For completness we briefly introduce in Sec. II the forward and backward master equation in different forms using the backward form for the calculation of time-dependent conditional average values. Hänggi and Thomas[1] have pointed out that the backward form of the master equation is especially suited for this purpose. We then develop a new method for calculating this quantity to any order in the expansion parameter Ω by solving a corresponding set of first-order linear partial differential equations. Finally, we give two examples and discuss the relationship of the presented method with the extensive and pioneering work by van Kampen in this field.

II. FORWARD AND BACKWARD FORM OF THE MASTER EQUATION

Let us consider a physical process which can be described by a time-dependent distribution function (TDF) $h(x,t \mid x_0)$. This TDF can, e.g., either describe the time-dependent velocity distribution of a labeled Brownian particle or the time-dependent distribution of the number of electrons in an Alkemade diode subject to the initial condition $h(x,t=0 \mid x_0)=\delta(x-x_0)$. Here we restrict ourselves to processes, which can be described by a homogeneous Markov process of a single variable x (x being continuous or discrete but unbounded, $-\infty \leq x \leq \infty$). Furthermore, we assume that successive events are statistically uncorrelated and can be described by a time-independent transition probability $W_\Omega(x \to x')$.

Let us introduce the following quantities: $h(x,t \mid x_0)$ is the probability to find the system at time t in the state x when it has been at time $t=0$ in the state x_0; $h(x,t=0 \mid x_0)=\delta(x-x_0)$ is the initial condition; $W_\Omega(x \to x')$ is the time-independent transition probability per unit time from x to x' (the subscript Ω refers to an explicit dependence on a given parameter Ω, which may be, e.g., a mass ratio or a volume); $\exp[-P_\Omega(x_0)t]$ is the probability that during a time interval t no transition takes place, with $P_\Omega(x) \equiv \int W_\Omega(x \to x')dx'$.

In order to obtain an equation for the TDF $h(x,t \mid x_0)$ the usual assumptions for the possibilities of a change are considered.

No transition takes place. The system is at $t=0$ in the state x_0 and has the probability $\exp[-P_\Omega(x_0)t]\delta(x-x_0)$ to remain in this state.

There are transitions. For this process two equivalent descriptions are possible. They are as follows.

(i) Up to t_1 the system evolves according to the probability $h(x_1,t_1 \mid x_0)$, changes its state from x_1 to x in the time interval (t_1, t_1+dt_1) with a time-independent transition probability $W_\Omega(x_1 \to x)$ and then remains in this state. The probability for this process is given by

$$\int dx_1 \int_{t_1=0}^{t_1=t} dt_1 h(x_1,t_1 \mid x_0) W_\Omega(x_1 \to x) \times \exp[-P_\Omega(x)(t-t_1)] . \quad (1a)$$

(ii) Up to t_1 the system remains in the initial state, changes its state from x_0 to x_1 in the time interval (t_1, t_1+dt_1) with the probability $W_\Omega(x_0 \to x_1)$, and then evolves according to the probability $h(x,t-t_1 \mid x_1)$. The probability for this process is given by

$$\int dx_1 \int_{t_1=0}^{t_1=t} dt_1 \exp[-P_\Omega(x_0)t_1] W_\Omega(x_0 \to x_1) \times h(x,t-t_1 \mid x_1) . \quad (1b)$$

Using either Eq. (1a) or (1b) we arrive at the equivalent equations for the TDF $h(x,t \mid x_0)$,

$$h_f(x,t \mid x_0) = \exp[-P_\Omega(x_0)t]\delta(x-x_0) + \int dx_1 \int_{t_1=0}^{t_1=t} dt_1 h_f(x_1,t_1 \mid x_0) W_\Omega(x_1 \to x) \exp[-P_\Omega(x)(t-t_1)] \quad (2a)$$

and

$$h_b(x,t \mid x_0) = \exp[-P_\Omega(x_0)t]\delta(x-x_0) + \int dx_1 \int_{t_1=0}^{t_1=t} dt_1 \exp[-P_\Omega(x_0)t_1] W_\Omega(x_0 \to x_1) h_b(x,t-t_1 \mid x_1) . \quad (2b)$$

Both equations can be transformed to the usual form of an integro-differential equation yielding, respectively,

$$\frac{\partial h_f(x,t \mid x_0)}{\partial t} = -P_\Omega(x) h_f(x,t \mid x_0) + \int W_\Omega(x_1 \to x) h_f(x_1,t \mid x_0) dx_1 \quad (3a)$$

and

$$\frac{\partial h_b(x,t \mid x_0)}{\partial t} = -P_\Omega(x_0) h_b(x,t \mid x_0) + \int W_\Omega(x_0 \to x_1) h_b(x,t \mid x_1) dx_1 , \quad (3b)$$

where both equations are solved subject to the initial condition

$$h_f(x,t=0 \mid x_0) = h_b(x,t=0 \mid x_0) = \delta(x-x_0) . \quad (4)$$

Equations (3a) and (3b) represent the well-known form of the forward and backward master equation, respectively.

From a physical point of view one is either interested in the solution of the master equation itself, yielding the time-dependent distribution function for this process, or in the time evolution of an averaged quantity only. This latter quantity cannot be obtained in general from the forward master equation. Of course, if the TDF $h(x,t \mid x_0)$ is known explicitly, all conditional averages can be calculated via the following relation:

$$\langle f(x) \mid x_0 \rangle_t \equiv \chi(x_0,t) \equiv \int f(x) h(x,t \mid x_0) dx \quad (5a)$$

with the initial condition

$$\chi(x_0,t=0) = \int f(x)\delta(x-x_0)dx = f(x_0) . \quad (5b)$$

If one is interested in the time evolution of an averaged quantity $\chi(x_0,t)$ only, it is appropriate to use the backward form of the master equation directly,[1] yielding

$$\frac{\partial\chi(x_0,t)}{\partial t}+P_\Omega(x_0)\chi(x_0,t) = \int W_\Omega(x_0\to x_1)\chi(x_1,t)dx_1 \ . \quad (6a)$$

This equation which is our starting point for Secs. III–VII is again an integro-differential equation, but now for the conditional average quantity $\chi(x_0,t)$ itself, and has to be solved subject to the initial condition

$$\chi(x_0,t=0)=f(x_0) \ . \quad (6b)$$

In his pioneering paper van Kampen[7] has derived a method for solving Eq. (3a) using a rather general dependence of the transition probability $W_\Omega(x_0\to x_1)$ on the parameter Ω. In his first approximation, the linear noise approximation, he arrived at the linear Fokker-Planck equation with time-dependent coefficients.

As an alternative way we will present in Secs. III–VII a systematic expansion of an averaged quantity $\chi(x_0,t)$ in the parameter Ω using the transport equation [see Eq. (6a)].

III. GENERAL EXPANSION METHOD FOR $\chi(x_0,\tau)$

Following van Kampen[7,8] we assume that the transition probability $W_\Omega(x\to x')$ can be written in the form

$$W_\Omega(x\to x')=F(\Omega)\sum_{k=0}^{\infty}\frac{1}{\Omega^k}W_k[x,\Omega(x'-x)] \ , \quad (7)$$

where $F(\Omega)$ is an arbitrary function. The parameter Ω is a size parameter and its precise definition depends on the system considered. In Eq. (7) we expressed the transition probability in terms of the intensive variable x, whereas van Kampen[7] used a dependence on an extensive variable. If we expand $\chi(x_1,t)$ in a Taylor series

$$\chi(x_1,t)=\sum_{n=0}^{\infty}\frac{(x_1-x_0)^n}{n!}\chi^{(n)}(x_0,t) \quad (8a)$$

we obtain, using Eq. (6a),

$$\frac{\partial\chi(x_0,t)}{\partial t}=\sum_{n=1}^{\infty}\frac{K_n(x_0)}{n!}\chi^{(n)}(x_0,t) \ , \quad (8b)$$

where we have introduced the jump moments

$$K_n(x_0)=\int W_\Omega(x_0\to x_1)(x_1-x_0)^n dx_1 \quad (9)$$

with

$$K_0(x_0)=P_\Omega(x_0) \ .$$

With the aid of Eq. (7) the jump moments can be expressed in the form

$$K_n(x_0)=\frac{F(\Omega)}{\Omega^{n+1}}\sum_{k=0}^{\infty}\frac{\alpha_{n,k}(x_0)}{\Omega^k} \quad (10a)$$

with

$$\alpha_{n,k}(x_0)\equiv\int W_k(x_0,y)y^n dy \ . \quad (10b)$$

Next we introduce a new time scale in our master equation for averages [see Eq. (8b)]

$$\frac{F(\Omega)}{\Omega^2}t=\tau, \quad \chi(x,t)=\tilde{\chi}(x,\tau) \ . \quad (11)$$

Dropping the tilde in the following one gives

$$\frac{\partial\chi(x_0,\tau)}{\partial\tau}=\sum_{n=1}^{\infty}\sum_{k=0}^{\infty}\frac{1}{\Omega^{n+k-1}}\frac{\alpha_{n,k}(x_0)}{n!}\chi^{(n)}(x_0,\tau) \ , \quad (12)$$

where $\chi^{(n)}(x_0,\tau)$ denotes the nth derivative of $\chi(x_0,\tau)$ with respect to x_0. As the kernel of the integro-differential equation [Eq. (6a)] depends on the parameter Ω, the average quantity $\chi(x_0,\tau)$ depends on Ω too. Therefore we expand $\chi(x_0,\tau)$ in powers of $1/\Omega$,

$$\chi(x_0,\tau)=\sum_{l=0}^{\infty}\frac{1}{\Omega^l}\chi_l(x_0,\tau) \ , \quad (13)$$

where the χ_l's are now independent of Ω and have to be determined by Eq. (12). Notice, that due to the initial condition (6b) one has

$$\chi(x_0,\tau=0)=f(x_0)=\sum_{l=0}^{\infty}\frac{1}{\Omega^l}\chi_l(x_0,\tau=0) \ , \quad (14)$$

yielding the new initial conditions

$$\chi_0(x_0,\tau=0)=f(x_0) \ , \quad (15a)$$

$$\chi_l(x_0,\tau=0)=0 \ \text{ for } \ l\geq 1 \ . \quad (15b)$$

Inserting Eq. (13) into Eq. (12) one obtains

$$\sum_{l=0}^{\infty}\frac{1}{\Omega^l}\frac{\partial\chi_l(x_0,\tau)}{\partial\tau} = \sum_{n=1}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\frac{1}{\Omega^{n+k+l-1}}\frac{\alpha_{n,k}(x_0)}{n!}\chi_l^{(n)}(x_0,\tau) \ . \quad (16)$$

Now performing an index transformation and comparing equal powers in $1/\Omega^l$ one has

$$\frac{\partial\chi_l(x_0,\tau)}{\partial\tau}=\sum_{n=1}^{l+1}\sum_{k=0}^{l+1-n}\frac{\alpha_{n,k}(x_0)}{n!}\chi_{l+1-n-k}^{(n)}(x_0,\tau) \ , \quad l=0,1,\ldots \ . \quad (17)$$

Rearranging the terms on the right-hand side (rhs) of Eq. (17) one can cast these equations into a more convenient form

$$\frac{\partial\chi_0(x_0,\tau)}{\partial\tau}-\alpha_{1,0}(x_0)\chi_0^{(1)}(x_0,\tau)=0 \ , \quad (18a)$$

$$\frac{\partial\chi_l(x_0,\tau)}{\partial\tau}-\alpha_{1,0}(x_0)\chi_l^{(1)}(x_0,\tau)=H_l(x_0,\tau) \quad \text{for } l\geq 1 \quad (18b)$$

with

$$H_l(x_0,\tau)=\sum_{s=2}^{l+1}\sum_{k=1}^{s}\frac{\alpha_{k,s-k}(x_0)}{k!}\chi_{l+1-s}^{(k)}(x_0,\tau) \ . \quad (18c)$$

Equations (18a) and (18b) have to be solved subject to the initial conditions [Eqs. (15a) and (15b), respectively].

Notice that $H_l(x_0,\tau)$ contains the derivatives of functions $\chi_k(x_0,\tau)$ with $k<l$ only and therefore Eqs. (18a) and (18b) can be solved in a successive way, meaning that higher approximations do not change lower approximations. Once the functions $\chi_l(x_0,\tau)$ are determined one ob-

tains a systematic expansion of $\chi(x_0,\tau)$ in powers of $1/\Omega$ using Eq. (13).

IV. DETERMINATION OF THE COEFFICIENTS $\chi_l(x_0,\tau)$

In order to solve Eqs. (18a) and (18b) subject to the initial conditions [Eqs. (15a) and (15b), respectively], we have to consider two different cases for the coefficient $\alpha_{1,0}(x_0)$.

(i) $\alpha_{1,0}(x_0)=0$. In this case the solutions of Eqs. (18a) and (18b) are trivially given by

$$\chi_0(x_0,\tau)=f(x_0)\ , \tag{19a}$$

$$\chi_l(x_0,\tau)=\int_0^\tau H_l(x_0,\tau')d\tau'\ . \tag{19b}$$

A master equation, in which the first jump moment $\alpha_{1,0}(x_0)$ is identical to zero is called a master equation of diffusion type.[8] This name becomes more obvious if we consider the first two terms in our Ω expansion [see Eq. (13)]. One has, using Eqs. (19a), (19b), and (18c),

$$\langle f(x)\,|\,x_0\rangle_\tau\equiv\chi(x_0,\tau)=f(x_0)+\frac{\tau}{\Omega}\left[\frac{\alpha_{1,1}}{1!}f^{(1)}(x_0)+\frac{\alpha_{2,0}}{2!}f^{(2)}(x_0)\right]+O\left[\frac{1}{\Omega^2}\right]\ . \tag{20}$$

Since $f(x_0)$ is an arbitrary function one can calculate from this equation the variance σ^2 up to the order $1/\Omega$

$$\sigma^2(x_0,\tau)\equiv\langle x^2\,|\,x_0\rangle_\tau-\langle x\,|\,x_0\rangle_\tau^2 =\frac{\tau}{\Omega}\alpha_{2,0}(x_0)+O\left[\frac{1}{\Omega^2}\right]\ . \tag{21}$$

According to Eq. (21), the fluctuations in this system grow linearly with time as in Brownian motion, which justifies the name "diffusion type." In Sec. VII we will give an example for such a diffusion process.

(ii) $\alpha_{1,0}(x_0)\neq 0$. This is the more complicated case since we have to solve the linear partial differential equations [Eqs. (18a) and (18b)] with a nonvanishing coefficient $\alpha_{1,0}(x_0)$ subject to the initial conditions [Eqs. (15a) and (15b)]. Let us first consider Eq. (18a)

$$\frac{\partial\chi_0(x_0,\tau)}{\partial\tau}-\alpha_{1,0}(x_0)\frac{\partial\chi_0(x_0,\tau)}{\partial x_0}=0 \tag{22a}$$

with the initial condition

$$\chi_0(x_0,\tau=0)=f(x_0)\ . \tag{22b}$$

Equation (22a) represents a first-order linear partial differential equation, which can be solved by the standard method of characteristics, solving the set of ordinary differential equations

$$\frac{d\tau}{dp}=1,\quad \frac{dx_0}{dp}=-\alpha_{1,0}(x_0),\quad \frac{d\chi_0}{dp}=0\ . \tag{23}$$

This yields

$$\tau(p)=\tau(0)+p,\quad x_0(p)=G^{-1}(p+G(x_0(0)))\ ,$$
$$\chi_0[p]=\chi_0[0]\ , \tag{24}$$

where $G^{-1}(x)$ is the inverse function of $G(x)$ defined by

$$G(x_0)\equiv-\int\frac{dx_0}{\alpha_{1,0}(x_0)}\ . \tag{25}$$

In order to satisfy the initial condition [Eq. (22b)] we have to select the following initial values:

$$\tau(0)=0,\quad x_0(0)=q,\quad \chi_0[0]=f(q)\ . \tag{26}$$

Inserting Eq. (26) into Eq. (24) yields the desired relations

$$p=\tau,\quad q=G^{-1}(G(x_0)-\tau)\equiv\bar{x}(\tau) \tag{27a}$$

and

$$\chi_0(x_0,\tau)=f(\bar{x}(\tau)) \tag{27b}$$

which shows that $\chi_0(x_0,\tau)$ depends on τ through $\bar{x}(\tau)$ only.

Obviously Eq. (27a) is equivalent to the solution of the ordinary differential equation

$$\frac{d\bar{x}}{d\tau}=\alpha_{1,0}(\bar{x}) \tag{28a}$$

with the initial condition

$$\bar{x}(0)=x_0\ . \tag{28b}$$

Equation (28a) represents the macroscopic equation of the system; this feature will become clear later. Van Kampen[7,8] has derived Eq. (28a) using an expansion method for the TDF itself. For a detailed discussion of the macroscopic equation we refer to van Kampen. For our present discussion we suppose that the solution of the macroscopic equation is stable, which implies

$$\frac{d\alpha_{1,0}(\bar{x})}{d\bar{x}}\equiv\alpha'_{1,0}(\bar{x})<0\ \text{ for all }\bar{x}\ . \tag{29}$$

In the following we will need the derivative of $\bar{x}$ with respect to the initial condition x_0

$$\frac{d\bar{x}}{dx_0}=\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)} \tag{30}$$

which is a consequence of Eq. (27a), too. Next we have to solve Eq. (18b)

$$\frac{\partial\chi_l(x_0,\tau)}{\partial\tau}-\alpha_{1,0}(x_0)\frac{\partial\chi_l(x_0,\tau)}{\partial x_0}=H_l(x_0,\tau)\ ,\qquad l=1,2,\ldots \tag{31a}$$

with the initial condition

$$\chi_l(x_0,\tau=0)=0\ . \tag{31b}$$

Using the method of characteristics again we now have to solve the set of ordinary differential equations

$$\frac{d\tau}{dp}=1,\quad \frac{dx_0}{dp}=-\alpha_{1,0}(x_0),\quad \frac{d\chi_l}{dp}=H_l\ , \tag{32}$$

yielding

$$\tau(p)=\tau(0)+p,\quad x_0(p)=G^{-1}(p+G(x_0(0)))\ ,$$
$$\chi_l[p]=\chi_l[0]+\int_0^p H_l(x_0(p'),\tau(p'))dp'\ , \tag{33}$$

where we have to select

$$\tau(0)=0,\quad x_0(0)=q,\quad \chi_l[0]=0\ , \tag{34}$$

in order to satisfy the initial condition Eq. (31b). We finally obtain

$$p=\tau,\quad q=G^{-1}(G(x_0)-\tau)\equiv\bar{x}(\tau)\ , \tag{35a}$$

and

$$\chi_l(x_0,\tau)=\int_0^\tau H_l(\bar{x}(\tau-s),s)ds\ , \tag{35b}$$

where Eq. (35b) represents the solution of Eq. (31a) subject to the initial condition [Eq. (31b)]. The expression for $\chi_l(x_0,\tau)$ can be simplified considerably, if one expresses the functions $H_l(x_0,\tau)$ in terms of the independent variables $x_0,\bar{x}$ which means that $H_l(x_0,\tau)$ depends on τ through $\bar{x}(\tau)$ only (for a proof see Appendix A). In order to distinguish both expressions we write

$$H_l(x_0,\tau)=H_l[x_0,\bar{x}] \tag{36}$$

using square brackets if H_l (or any other function) is expressed by the independent variables $x_0,\bar{x}$. It is shown in Appendix A that $\chi_l(x_0,\tau)$ can be expressed by

$$\chi_l(x_0,\tau)=\chi_l[x_0,\bar{x}]=\int_{x_0}^{\bar{x}}\frac{H_l[y,\bar{x}]}{\alpha_{1,0}(y)}dy \tag{37}$$

representing the solutions of Eq. (31a). Using Eqs. (37) and (13) we conclude that in any average quantity $\chi_l(x_0,\tau)$ time enters through the solution $\bar{x}$ of the macroscopic equation (28a) only.

V. EXPLICIT EXPRESSION FOR $\chi_l(x_0,\tau)$

In this section we want to give the exact expression for an arbitrary average $\chi(x_0,\tau)$ including the order $1/\Omega$.

According to Eq. (18c) $H_l(x_0,\tau)$ is given by

$$H_l(x_0,\tau)=\alpha_{1,1}(x_0)\frac{\partial\chi_0(x_0,\tau)}{\partial x_0}+\frac{\alpha_{2,0}(x_0)}{2}\frac{\partial^2\chi_0(x_0,\tau)}{\partial x_0^2}\ . \tag{38}$$

Using Eqs. (27b) and (30) we obtain for the derivatives of $\chi_0(x_0,\tau)$

$$\chi_0(x_0,\tau)=\chi_0[x_0,\bar{x}]=f(\bar{x})\ , \tag{39a}$$

$$\frac{\partial\chi_0(x_0,\tau)}{\partial x_0}=f'(\bar{x})\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)}\ , \tag{39b}$$

$$\frac{\partial^2\chi_0(x_0,\tau)}{\partial x_0^2}=f''(\bar{x})\left[\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)}\right]^2+f'(\bar{x})\alpha_{1,0}(\bar{x})\times\left[\frac{\alpha'_{1,0}(\bar{x})-\alpha'_{1,0}(x_0)}{\alpha_{1,0}^2(x_0)}\right]\ , \tag{39c}$$

where the prime indicates derivatives with respect to the argument of the functions. Inserting these relations into Eqs. (38) and (37), respectively, one obtains for $\chi_1(x_0,\tau)$

$$\chi_1(x_0,\tau)=\chi_1[x_0,\bar{x}]=f''(\bar{x})\frac{\sigma^2_{\rm scal}[x_0,\bar{x}]}{2}+f'(\bar{x})\Phi_1[x_0,\bar{x}]\ , \tag{40}$$

where we have introduced the following functions:

$$\sigma^2_{\rm scal}[x_0,\bar{x}]=\alpha^2_{1,0}(\bar{x})\int_{x_0}^{\bar{x}}\frac{\alpha_{2,0}(y)}{\alpha^3_{1,0}(y)}dy\ , \tag{41a}$$

$$\Phi_1[x_0,\bar{x}]=\alpha_{1,0}(\bar{x})\int_{x_0}^{\bar{x}}\left[\frac{\alpha_{1,1}(y)}{\alpha^2_{1,0}(y)}+\frac{\alpha_{2,0}(y)}{2}\left[\frac{\alpha'_{1,0}(\bar{x})-\alpha'_{1,0}(y)}{\alpha^3_{1,0}(y)}\right]\right]dy\ . \tag{41b}$$

Inserting Eq. (40) into Eq. (13) we arrive at the following relation:

$$\langle f(x)\,|\,x_0\rangle_\tau\equiv\chi(x_0,\tau)=\chi[x_0,\bar{x}]=f(\bar{x})+\frac{1}{\Omega}\left[f''(\bar{x})\frac{\sigma^2_{\rm scal}[x_0,\bar{x}]}{2}+f'(\bar{x})\Phi_1[x_0,\bar{x}]\right]+O\left[\frac{1}{\Omega^2}\right] \tag{42}$$

yielding an exact expansion for an arbitrary time-dependent mean value $\chi_0(x_0,\tau)$ up to the order $1/\Omega$. Equation (42) enables us to calculate the variance $\sigma^2(x_0,\tau)$ of the system choosing for $f(x_0)$ the function x_0 and x_0^2, respectively,

$$\langle x\,|\,x_0\rangle_\tau=\bar{x}+\frac{1}{\Omega}\Phi_1[x_0,\bar{x}]+O\left[\frac{1}{\Omega^2}\right]\ , \tag{43a}$$

$$\langle x^2\,|\,x_0\rangle_\tau=\bar{x}^2+\frac{1}{\Omega}(\sigma^2_{\rm scal}[x_0,\bar{x}]+2\bar{x}\Phi_1[x_0,\bar{x}])+O\left[\frac{1}{\Omega^2}\right]\ . \tag{43b}$$

This implies

$$\sigma^2(x_0,\tau)\equiv\langle x^2\,|\,x_0\rangle_\tau-\langle x\,|\,x_0\rangle_\tau^2=\frac{1}{\Omega}\sigma^2_{\rm scal}[x_0,\bar{x}]+O\left[\frac{1}{\Omega^2}\right]\ . \tag{43c}$$

Now the meaning of $\sigma^2_{\rm scal}$ as a scaled variance becomes clear. Taking the time derivative of Eq. (41a) one obtains a differential equation for the scaled variance

$$\frac{d\sigma^2_{\rm scal}}{d\tau}=2\alpha'_{1,0}(\bar{x})\sigma^2_{\rm scal}+\alpha_{2,0}(\bar{x}) \tag{44a}$$

which has to be solved subject to the initial condition

$$\sigma^2_{\rm scal}(x_0,\tau=0)=0\ . \tag{44b}$$

Equations (44a) and (44b) agree with the results obtained by van Kampen,[7,8] whereas the function $\Phi_1[x_0,\bar{x}]$ [see Eqs. (42) and (41b)] does not appear in his linear noise approximation. In order to obtain a correct expansion of an averaged quantity one has to use within van Kampen's method higher-order approximations which means solving a set of coupled differential equations.[12]

VI. LINEAR NOISE APPROXIMATION EMERGENCE OF THE GAUSSIAN DISTRIBUTION

In principle, one could calculate higher-order terms of Eq. (42) yielding rather long explicit expressions for $\chi_2,\chi_3,\ldots$, etc. Since in many examples calculations simplify considerably, we restrict ourselves to the first coefficients χ_0,χ_1 given in Sec. V.

In this section we focus our attention on the general structure of Eq. (42), which is given by

$$\begin{aligned}\langle f(x)\,|\,x_0\rangle_\tau\equiv\chi(x_0,\tau)=f(\bar{x})&+\frac{1}{\Omega}[f^{(2)}(\bar{x})\chi_{1,2}+f^{(1)}(\bar{x})\chi_{1,1}]\\&+\frac{1}{\Omega^2}[f^{(4)}(\bar{x})\chi_{2,4}+f^{(3)}(\bar{x})\chi_{2,3}+f^{(2)}(\bar{x})\chi_{2,2}+f^{(1)}(\bar{x})\chi_{2,1}]\\&+\frac{1}{\Omega^3}[f^{(6)}(\bar{x})\chi_{3,6}+\cdots+f^{(1)}(\bar{x})\chi_{3,1}]+O\left[\frac{1}{\Omega^4}\right]\ ,\end{aligned} \tag{45}$$

where $f^{(n)}(\bar{x})$ denotes the nth derivative of $f(\bar{x})$ with respect to the argument $\bar{x}$. For a proof of this equation see Appendix B. Equation (45) can be written in a closed form

$$\langle f(x)\,|\,x_0\rangle_\tau=f(\bar{x})+\sum_{k=1}^{\infty}\frac{1}{\Omega^k}\sum_{l=0}^{2k-1}f^{(2k-l)}(\bar{x})\chi_{k,2k-l}[x_0,\bar{x}] \tag{46}$$

the coefficients $\chi_{k,2k-l}$ being determined with the aid of Eqs. (37), (18c), and (13), respectively. The coefficients $\chi_{1,2}$ and $\chi_{1,1}$ have already been calculated in the previous sections and are given by

$$\chi_{1,2}[x_0,\bar{x}]=\tfrac{1}{2}\sigma^2_{\rm scal}[x_0,\bar{x}]\ , \tag{47a}$$

$$\chi_{1,1}[x_0,\bar{x}]=\Phi_1[x_0,\bar{x}]\ . \tag{47b}$$

In Appendix B we show that the coefficients $\chi_{k,2k}$ can be calculated very simply yielding

$$\chi_{k,2k}[x_0,\bar{x}]=\frac{1}{k!}(\chi_{1,2}[x_0,\bar{x}])^k\ . \tag{47c}$$

Inserting this expression into Eqs. (47a) and (46) we obtain

$$\langle f(x)\,|\,x_0\rangle_\tau=f(\bar{x})+\sum_{k=1}^{\infty}\frac{f^{(2k)}(\bar{x})}{k!}\left[\frac{\sigma^2_{\rm scal}}{2\Omega}\right]^k+\sum_{k=1}^{\infty}\frac{1}{\Omega^k}\sum_{l=1}^{2k-1}f^{(2k-l)}(\bar{x})\chi_{k,2k-l}[x_0,\bar{x}]\ . \tag{48}$$

If we neglect the third term on the rhs of Eq. (48) we get the following relation:

$$\langle f(x)\,|\,x_0\rangle_\tau\approx f(\bar{x})+\sum_{k=1}^{\infty}\frac{f^{(2k)}(\bar{x})}{k!}\left[\frac{\sigma^2_{\rm scal}}{2\Omega}\right]^k \tag{49}$$

which can be obtained in an alternative way using in Eqs. (5a) and (5b) a normalized Gaussian distribution function

$$h(x',\tau\,|\,x_0)=\left[\frac{\Omega}{2\pi\sigma^2_{\rm scal}}\right]^{1/2}\exp\left[-\frac{\Omega(x'-\bar{x})^2}{2\sigma^2_{\rm scal}}\right] \tag{50}$$

with time-dependent mean and variance given by Eqs. (41a) and (27a), respectively. In the linear noise approximation the distribution function $h(x',\tau\,|\,x_0)$ is derived by van Kampen[8] as a solution of a Fokker-Planck equation with time-dependent coefficients, yielding an identical expression to Eq. (50).

From a mathematical point of view there is no *a priori* justification for neglecting the third term on the rhs of Eq. (48), since it contains terms of the same order in $1/\Omega$ as the second one. To elucidate this, let us consider a system where the parameter $1/\Omega$ can be made arbitrarily small (cf Rayleigh piston, where $1/\Omega$ has the meaning of a mass ratio). In this case it is sufficient to consider terms up to the power $1/\Omega$ only neglecting higher-order terms both in Eqs. (45) and (49). We obtain in our approximation [see Eq. (45)]

$$\langle f(x)\,|\,x_0\rangle_\tau\approx f(\bar{x})+\frac{1}{\Omega}\left[f''(\bar{x})\frac{\sigma^2_{\rm scal}[x_0,\bar{x}]}{2}+f'(\bar{x})\Phi_1[x_0,\bar{x}]\right] \tag{51}$$

whereas in the linear noise approximation [see Eq. (49)] one has

$$\langle f(x)\,|\,x_0\rangle_\tau \approx f(\bar{x}) + \frac{1}{\Omega} f''(\bar{x}) \frac{\sigma^2_{\text{scal}}[x_0,\bar{x}]}{2} \quad . \tag{52}$$

This shows most clearly that, e.g., the mean velocity or mean energy of a heavy particle moving in a dilute gas (Rayleigh piston) cannot be described correctly within the linear noise approximation and one has to use Eq. (51) instead of Eq. (52). We conclude that, in general, the linear noise approximation yields incorrect results, if it is used to expand averages of an arbitrary function in powers of $1/\Omega$.[12]

VII. EXAMPLES

A. Brownian particle and diffusion process (Ref. 13)

For an exact treatment of a diffusion process within the uncorrelated binary-collision model we refer to our earlier papers.[14,15] Here we briefly present the results for a special diffusion process, where all jump moments $\alpha_{n,k}$ but the second one $\alpha_{2,0}$ vanish.

According to Eq. (18c) one has

$$H_l(x_0,\tau) = \frac{\alpha_{2,0}}{2} \chi^{(2)}_{l-1}(x_0,\tau) \tag{53}$$

yielding for $\chi_l(x_0,\tau)$ in the case of a constant coefficient $\alpha_{2,0}$ [see Eqs. (19a) and (19b)]

$$\chi_l(x_0,\tau) = \left[\frac{\alpha_{2,0}}{2}\right]^l \frac{\tau^l}{l!} f^{(2l)}(x_0) \tag{54}$$

and for $\chi(x_0,\tau)$ [see Eq. (13)]

$$\begin{aligned}\chi(x_0,\tau) &\equiv \langle f(x)\,|\,x_0\rangle_\tau \\ &= f(x_0) + \sum_{k=1}^{\infty} \frac{f^{(2k)}(x_0)}{k!} \left[\frac{\alpha_{2,0}\tau}{2\Omega}\right]^k \quad .\end{aligned} \tag{55}$$

This result can be obtained too using Eq. (5a) and the normalized Gaussian distribution function

$$\begin{aligned}h(x',\tau\,|\,x_0) = &\left[\frac{\Omega}{2\pi\alpha_{2,0}\tau}\right]^{1/2} \\ &\times \exp\left[-\frac{\Omega(x'-x_0)^2}{2\alpha_{2,0}\tau}\right]\end{aligned} \tag{56}$$

which appears in the normal treatment of the master equation (the Kramers-Moyal[16] expansion) as the fundamental solution of the diffusion equation.

B. Alkemade diode

A beautiful application of the master equation for the Alkemade diode,[10] is given by van Kampen[11] and in the following we refer to this paper. In proper time units the master equation for the distribution function is given by

$$\begin{aligned}\frac{\partial h(N,t\,|\,N_0)}{\partial t} &= -P_\Omega(N) h(N,t\,|\,N_0) \\ &\quad + \int W_\Omega(N'\to N) h(N',t\,|\,N_0)\,dN' \quad .\end{aligned} \tag{57a}$$

The corresponding equation for an arbitrary average $\psi(N_0,t)$ reads

$$\begin{aligned}\frac{\partial \psi(N_0,t)}{\partial t} + P_\Omega(N_0,t)\psi(N_0,t) \\ = \int W_\Omega(N_0\to N')\psi(N',t)\,dN'\end{aligned} \tag{57b}$$

with

$$\begin{aligned}W_\Omega(N_0\to N') &= \delta(N'-N_0+1) \\ &\quad + \xi e^{-N_0/\Omega}\delta(N'-N_0-1) \quad , \\ \xi \equiv e^{\eta-1/2\Omega}, &\quad \eta \equiv \frac{W_1-W_2}{kT} \quad ,\end{aligned} \tag{57c}$$

where η is the ratio of the difference of the working functions of the diode to the thermal energy. Since one expects for the equilibrium value

$$\lim_{t\to\infty} \langle N\,|\,N_0\rangle_t = N_\infty = \Omega\eta = \langle N_0\rangle^{\text{eq}} \tag{58}$$

we perform the following variable transformation:

$$N_0 = N_\infty + \tilde{N}_0, \quad \psi(N_0,t) = \tilde{\psi}(\tilde{N}_0,t) \quad . \tag{59}$$

This transformation will merely simplify our calculations and is not essential for our considerations. In this new variables Eq. (57b) reads

$$\begin{aligned}\frac{\partial \tilde{\psi}(\tilde{N}_0,t)}{\partial t} + \tilde{P}_\Omega(\tilde{N}_0)\tilde{\psi}(\tilde{N}_0,t) \\ = \int \tilde{W}_\Omega(\tilde{N}_0\to\tilde{N}')\tilde{\psi}(\tilde{N}',t)\,d\tilde{N}'\end{aligned} \tag{60}$$

with

$$\begin{aligned}\tilde{W}_\Omega(\tilde{N}_0\to\tilde{N}') &= \delta(\tilde{N}'-\tilde{N}_0+1) \\ &\quad + \exp\left[-\frac{1}{\Omega}(\tilde{N}_0+\tfrac{1}{2})\right]\delta(\tilde{N}'-\tilde{N}_0-1)\end{aligned} \tag{61}$$

and

$$\tilde{P}_\Omega(\tilde{N}_0) = \int \tilde{W}_\Omega(\tilde{N}_0\to\tilde{N}')\,d\tilde{N}' \quad . \tag{62}$$

If we now introduce the scaled variables

$$\begin{aligned}&\tilde{N}_0 = \Omega x_0, \quad \tilde{N}' = \Omega x', \quad d\tilde{N}' = \Omega\,dx' \quad , \\ &\tilde{\psi}(\tilde{N}_0,t) = \tilde{\psi}(\Omega x_0,t) = \chi(x_0,t) \quad , \\ &\chi(x_0,t=0) = f(x_0) \quad ,\end{aligned} \tag{63}$$

we obtain instead of Eq. (60)

$$\begin{aligned}\frac{\partial \chi(x_0,t)}{\partial t} + P_\Omega(x_0)\chi(x_0,t) \\ = \Omega \int W_\Omega(x_0\to x_1)\chi(x_1,t)\,dx_1\end{aligned} \tag{64}$$

with

$$\Omega W_\Omega(x_0\to x')=\Omega\left[\delta(\Omega(x'-x_0)+1)+\exp\left[-x_0-\frac{1}{2\Omega}\right]\delta(\Omega(x'-x_0)-1)\right]=F(\Omega)\sum_{k=0}^{\infty}\frac{1}{\Omega^k}W_k[x_0,\Omega(x'-x_0)]\ . \quad (65)$$

Since the transition probability has just the form we required in Sec. III our general method applies, yielding

$$W_0[x_0,\Omega(x'-x_0)]\equiv W_0(x_0,y)=\delta(y+1)+e^{-x_0}\delta(y-1)\ , \quad (66a)$$

$$W_k(x_0,y)=\frac{1}{k!}\left[-\frac{1}{2}\right]^k e^{-x_0}\delta(y-1)\quad \text{for } k\geq 1\ , \quad (66b)$$

$$F(\Omega)=\Omega,\quad \frac{t}{\Omega}=\tau\ . \quad (66c)$$

For the jump moments $\alpha_{n,k}(x_0)$ one obtains

$$\alpha_{n,k}(x_0)=(-1)^n\delta_{k,0}+\frac{1}{k!}\left[-\frac{1}{2}\right]^k e^{-x_0}\ . \quad (67)$$

In our special case the macroscopic equation

$$\frac{d\bar{x}}{d\tau}=\alpha_{1,0}(\bar{x})=-1+e^{-\bar{x}} \quad (68)$$

can readily be integrated, yielding

$$\bar{x}(\tau)=\ln(1+Ae^{-\tau}) \quad (69a)$$

with

$$A\equiv e^{x_0}-1\ . \quad (69b)$$

With the aid of Eqs. (69a), (67), (27b), and (37) the coefficients $\chi_l(x_0,\tau)$ in the expansion

$$\chi(x_0,\tau)=\sum_{l=0}^{\infty}\frac{1}{\Omega^l}\chi_l(x_0,\tau) \quad (70)$$

can be calculated by a number of straightforward integrations. We obtain, restricting ourselves to χ_0 and χ_1 only,

$$\chi_0(x_0,\tau)=f(\bar{x})\ , \quad (71a)$$

$$\chi_1(x_0,\tau)=f''(\bar{x})\frac{\sigma^2_{\rm scal}(x_0,\tau)}{2}+f'(\bar{x})\Phi_1(x_0,\tau) \quad (71b)$$

with

$$\sigma^2_{\rm scal}(x_0,\tau)=\frac{1}{(1+Ae^{-\tau})^2}[1+3Ae^{-\tau}+(\tau A^2-3A-1)e^{-2\tau}]\ , \quad (72a)$$

$$\Phi_1(x_0,\tau)=\frac{e^{-\tau}}{2(1+Ae^{-\tau})^2}[A\tau+(2A+1)(e^{-\tau}-1)] \quad (72b)$$

or using Eq. (70),

$$\chi(x_0,\tau)\equiv\langle f(x)\,|\,x_0\rangle_\tau=f(\bar{x})+\frac{1}{\Omega}\left[f''(\bar{x})\frac{\sigma^2_{\rm scal}(x_0,\tau)}{2}+f'(\bar{x})\Phi_1(x_0,\tau)\right]+O\left[\frac{1}{\Omega^2}\right]\ . \quad (73)$$

Since $f(x)$ is an arbitrary function, we obtain explicit expressions for both the time-dependent scaled average number of particles $\langle x\,|\,x_0\rangle_\tau$ and the variance $\sigma^2_{\rm scal}(x_0,\tau)$ up to the order $1/\Omega$

$$\frac{1}{\Omega}\langle\tilde{N}\,|\,\tilde{N}_0\rangle_\tau=\langle x\,|\,x_0\rangle_\tau=\bar{x}+\frac{1}{\Omega}\Phi_1(x_0,\tau)+O\left[\frac{1}{\Omega^2}\right]\ , \quad (74a)$$

$$\sigma^2(x_0,\tau)\equiv\langle x^2\,|\,x_0\rangle_\tau-\langle x\,|\,x_0\rangle^2_\tau=\frac{1}{\Omega}\sigma^2_{\rm scal}(x_0,\tau)+O\left[\frac{1}{\Omega^2}\right]. \quad (74b)$$

Whereas the explicit expression for the variance [see Eq. (72a)] has been derived previously by van Kampen using different arguments, the function $\Phi_1(x_0,\tau)$ present in Eq. (73) does not appear in his linear noise approximation.

Using a suggestion of Bernard and Callen, van Kampen[15] uses a shifted Gaussian distribution for $t=0$, which enables him to calculate an expression for $\Phi_1(x_0,\tau)$, which is in contradiction to our result, where we did not have to make any assumptions about the initial distribution. In order to show the importance of the Φ_1 term in the expansion to order $1/\Omega$ we briefly sketch the calculation of the autocorrelation function $\langle x_0\langle x\,|\,x_0\rangle_\tau\rangle^{\rm eq}$ and the calculation of the mean number of electrons for $\lim_{\tau\to\infty}\langle N\,|\,N_0\rangle_\tau$. To calculate the autocorrelation function we need the equilibrium moments $\langle x_0^n\rangle^{\rm eq}$. In our scheme we could, in principle, calculate any equilibrium moment to arbitrary order in $1/\Omega$ via Eq. (45), but this would not provide further insight and, therefore, we use in the following, the expressions given by van Kampen:

$$\langle x_0\rangle^{\rm eq}=\langle x_0^3\rangle^{\rm eq}=0\ ,\qquad \langle x_0^2\rangle^{\rm eq}=\frac{1}{\Omega}\ ,\quad \langle x_0^4\rangle^{\rm eq}=\frac{3}{\Omega^2}\ . \quad (75a)$$

Without any further calculation we can conclude, using Eq. (45), in connection with Eq. (47c), that

$$\langle x_0\rangle^{\rm eq}=0+O\left[\frac{1}{\Omega^2}\right],\quad \langle x_0^3\rangle^{\rm eq}=0+O\left[\frac{1}{\Omega^2}\right]\ ,$$
$$\langle x_0^2\rangle^{\rm eq}=\frac{1}{\Omega}+O\left[\frac{1}{\Omega^2}\right],\quad \langle x_0^4\rangle^{\rm eq}=\frac{3}{\Omega^2}+O\left[\frac{1}{\Omega^3}\right]\ , \quad (75b)$$

where we have used the following notation:

$$\lim_{\tau\to\infty}\langle x^n\,|\,x_0\rangle_\tau=\langle x_0^n\rangle^{\rm eq}\ . \tag{75c}$$

Expanding Eq. (74a) in terms of x_0 we obtain

$$\begin{aligned}\langle x\,|\,x_0\rangle_\tau=&(a_0+a_1x_0+a_2x_0^2+a_3x_0^3+a_4x_0^4+\cdots)\\&+\frac{1}{\Omega}(b_0+b_1x_0+b_2x_0^2+\cdots)\\&+\frac{1}{\Omega^2}(c_0+c_1x_0+\cdots)+O\left[\frac{1}{\Omega^3}\right]\end{aligned} \tag{76}$$

and for the correlation function using the equilibrium moments [see Eqs. (75a)]

$$\begin{aligned}\langle x_0\langle x\,|\,x_0\rangle_\tau\rangle^{\rm eq}=&\alpha_1\langle x_0^2\rangle^{\rm eq}\\&+\left[a_3\langle x_0^4\rangle^{\rm eq}+\frac{b_1}{\Omega}\langle x_0^2\rangle^{\rm eq}\right]\\&+O\left[\frac{1}{\Omega^3}\right]\ .\end{aligned} \tag{77}$$

Since the coefficients a_n and b_n are derivatives of $\bar{x}$ and $\Phi_1(x_0,\tau)$, respectively, one obtains

$$a_1=e^{-\tau}\ , \tag{78a}$$

$$a_3=\tfrac{1}{6}e^{-\tau}(1-e^{-\tau})(1-2e^{-\tau})\ , \tag{78b}$$

$$b_1=\tfrac{1}{2}(-2e^{-\tau}+\tau e^{-\tau}+4e^{-2\tau}-2e^{-3\tau})\ , \tag{78c}$$

yielding for the correlation function

$$\langle x_0\langle x\,|\,x_0\rangle_\tau\rangle^{\rm eq}=\frac{1}{\Omega}e^{-\tau}+\frac{1}{2\Omega^2}e^{-\tau}(-1+\tau+e^{-\tau})\ . \tag{79}$$

The physical content, especially the relationship of Eq. (79) to the fluctuation-dissipation theorem is discussed in detail by van Kampen, who pointed out to us that this equation agrees with the first two terms of his exact result.[17] We want to comment on the differences in the approach to the derivation of Eq. (79). Our result follows directly from the explicit expression for $\Phi_1(x_0,\tau)$ and is identical to the result derived by van Kampen using his approximation scheme near equilibrium rather than a direct nonequilibrium calculation within the linear noise approximation. To obtain this result within the expansion method described by van Kampen, higher-order terms than present in the linear noise approximation have to be included.

In the calculation of $\lim_{\tau\to\infty}\langle\tilde{N}\,|\,\tilde{N}_0\rangle_\tau$ the transformation $N_0=N_\infty+\tilde{N}_0$ [see Eq. (59)] is convenient for the computation of the autocorrelation function but, in principle, not necessary. Van Kampen[7] has shown that $\lim_{\tau\to\infty}\langle N\,|\,N_0\rangle_\tau$ calculated either within the linear noise approximation [see Eq. (80a)] or from equilibrium fluctuations [see Eq. (80b)] give different results, namely,

$$\lim_{\tau\to\infty}\langle N\,|\,N_0\rangle_\tau=\Omega\ln\xi=\Omega\eta-\tfrac{1}{2}\ , \tag{80a}$$

$$\lim_{\tau\to\infty}\langle N\,|\,N_0\rangle_\tau=\Omega\eta\ , \tag{80b}$$

where no use of the transformation [see Eq. (59)] has been made. To resolve this discrepancy within the linear noise approximation by van Kampen again higher approximations would have to be taken into account. Within our scheme, however, it becomes evident that the new term $\Phi_1(x_0,\tau)$ in Eq. (42) resolves this problem naturally yielding

$$\lim_{\tau\to\infty}\langle N\,|\,N_0\rangle_\tau=\Omega\ln\xi+\tfrac{1}{2}=\Omega\eta\ . \tag{81}$$

This is an advantage of calculating time-dependent averages of arbitrary functions directly, via our expansion method, yielding results accurate to the order $1/\Omega$ considered and therefore avoiding discrepancies between finite and infinite times again to the order $1/\Omega$ considered.

ACKNOWLEDGMENTS

We are grateful to M. Posch for discussions and competent help on mathematical problems. Furthermore, we want to thank Professor N. G. van Kampen for pointing out the importance of Ref. 9.

APPENDIX A

Here we want to prove that $H_l(x_0,\tau)$ can be expressed by the variables x_0 and $\bar{x}$. We start with Eq. (35b) for $l=1$

$$\chi_1(x_0,\tau)=\int_0^\tau H_1(\bar{x}(\tau-s),s)ds \tag{A1}$$

with the explicit expression for $H_1(x_0,\tau)$ [see Eq. (18c)]

$$\begin{aligned}H_1(x_0,\tau)=&\alpha_{1,1}(x_0)\frac{\partial\chi_0(x_0,\tau)}{\partial x_0}\\&+\tfrac{1}{2}\alpha_{2,0}(x_0)\frac{\partial^2\chi_0(x_0,\tau)}{\partial x_0^2}\ .\end{aligned} \tag{A2}$$

The function $\chi_0(x_0,\tau)$ has been calculated in Sec. IV yielding

$$\chi_0(x_0,\tau)=f(\bar{x}) \tag{A3}$$

which is a function of $\bar{x}$ only.

Inserting Eq. (A3) into (A2), and using the special relation [see Eq. (30)]

$$\frac{d\bar{x}}{dx_0}=\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)}\ ,$$

one can conclude that $H_1(x_0,\tau)$ can be expressed by the independent variables $x_0,\bar{x}$

$$H_1(x_0,\tau)=H_1[x_0,\bar{x}]\ . \tag{A4}$$

Next we substitute in Eq. (A1)

$$\begin{aligned}&\bar{x}(\tau-s)=G^{-1}(G(x_0)-\tau+s)=y\ ,\\&\frac{dy}{ds}=-\frac{d\bar{x}}{d\tau}=-\alpha_{1,0}(y)\ ,\end{aligned} \tag{A5}$$

yielding

$$\chi_1(x_0,\tau)=\int_{x_0}^{\bar{x}}\frac{H_1(y,G(y)-G(x_0)+\tau)}{\alpha_{1,0}(y)}dy\ . \tag{A6}$$

If we now use Eq. (A4) we can write

$$H_1(y,\tau)=H_1(y,G^{-1}(G(y)-\tau)) \tag{A7}$$

or

$$H_1(y,G(y)-G(x_0)+\tau)=H_1(y,G^{-1}(G(x_0)-\tau)) \\ =H_1(y,\bar{x}(\tau)) \ . \tag{A8}$$

This can be used in Eq. (A6) yielding

$$\chi_1(x_0,\tau)=\int_{x_0}^{\bar{x}}\frac{H_1[y,\bar{x}]}{\alpha_{1,0}(y)}dy=\chi_1[x_0,\bar{x}] \ , \tag{A9}$$

where we have shown that both $H_1(x_0,\tau)$ and $\chi_1(x_0,\tau)$ depend on τ through $\bar{x}(\tau)$ only. The proof for $l>1$ is simply given by induction keeping in mind that $H_l(x_0,\tau)$ depends on the derivatives of $\chi_0,\chi_1,\ldots,\chi_{l-1}$ only and not on χ_l. One finally arrives at the expression

$$\chi_l(x_0,\tau)=\chi_l[x_0,\bar{x}]=\int_{x_0}^{\bar{x}}\frac{H_l[y,\bar{x}]}{\alpha_{1,0}(y)}dy \tag{A10}$$

which we wanted to prove.

APPENDIX B

Here we want to give a proof for Eq. (47c). According to Eq. (37) we have to calculate the functions $\chi_l[x_0,\bar{x}]$

$$\chi_l[x_0,\bar{x}]=\int_{x_0}^{\bar{x}}\frac{H_l[y,\bar{x}]}{\alpha_{1,0}(y)}dy \ , \tag{B1}$$

where $H_l[x_0,\bar{x}]$ is given by [see Eq. (18c)]

$$H_l[x_0,\bar{x}]=\sum_{s=2}^{l+1}\sum_{k=1}^{s}\frac{\alpha_{k,s-k}(x_0)}{k!}\frac{d^k}{dx_0^k}\chi_{l+1-s}[x_0,\bar{x}] \ . \tag{B2}$$

Since $\bar{x}(\tau)$ depends on x_0 one has the following relation:

$$\chi_0^{(1)}(x_0,\tau)=\frac{d}{dx_0}\chi_0[x_0,\bar{x}]=\frac{\partial}{\partial x_0}\chi_0[x_0,\bar{x}] \\ +\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)}\frac{\partial}{\partial\bar{x}}\chi_0[x_0,\bar{x}] \ , \tag{B3}$$

where we have introduced the abbreviations

$$\chi_l^{(k)}(x_0,\tau)=\frac{\partial^k}{\partial x_0^k}\chi_l(x_0,\tau)=\frac{d^k}{dx_0^k}\chi_l[x_0,\bar{x}] \ . \tag{B4}$$

Let us first rearrange Eq. (B2)

$$H_l(x_0,\tau)=H_l[x_0,\bar{x}] \\ =\sum_{s=2}^{l+1}\frac{\alpha_{s,0}(x_0)}{s!}\chi_{l+1-s}^{(s)}(x_0,\tau) \\ +\sum_{s=2}^{l+1}\frac{\alpha_{s-1,1}(x_0)}{(s-1)!}\chi_{l+1-s}^{(s-1)}(x_0,\tau)+\cdots \ . \tag{B5}$$

According to Eq. (B5) the highest derivatives of the functions $\chi_{l+1-s}(x_0,\tau)$ with $2<s<l+1$, appear in the first term on the rhs only, all other terms giving lower derivatives of the same functions.

Next we want to calculate $\chi_2[x_0,\bar{x}]$ using the results for χ_0,χ_1 [see Eqs. (27b) and (40)]

$$\chi_0[x_0,\bar{x}]=f(\bar{x}) \ , \tag{B6}$$

$$\chi_1[x_0,\bar{x}]=f^{(2)}(\bar{x})\chi_{1,2}[x_0,\bar{x}]+f^{(1)}(\bar{x})\chi_{1,1}[x_0,\bar{x}] \tag{B7}$$

with

$$\chi_{1,2}=\frac{\sigma_{\text{scal}}^2}{2}, \ \chi_{1,1}=\Phi_1 \ .$$

Inserting these relations into Eq. (B5) we obtain with the aid of Eq. (B3)

$$H_2[x_0,\bar{x}]=\frac{\alpha_{2,0}(x_0)}{2}\left[\frac{\alpha_{1,0}(\bar{x})}{\alpha_{1,0}(x_0)}\right]^2\chi_{1,2}[x_0,\bar{x}]f^{(4)}(\bar{x}) \\ +O(f^{(3)}(\bar{x})) \ , \tag{B8}$$

where the symbol $O(f^{(l)}(\bar{x}))$ stands for all terms containing derivatives of $f(\bar{x})$ up to the order l only.

Using our general expression for $\chi_l[x_0,\bar{x}]$ [see Eq. (37)]

$$\chi_l[x_0,\bar{x}]=\int_{x_0}^{\bar{x}}\frac{H_l[y,\bar{x}]}{\alpha_{1,0}(y)}dy \tag{B9}$$

we obtain for χ_2

$$\chi_2[x_0,\bar{x}]=f^{(4)}(\bar{x})\frac{\alpha_{1,0}^2(\bar{x})}{2}\int_{x_0}^{\bar{x}}\frac{\alpha_{2,0}(y)}{\alpha_{1,0}^3(y)}\chi_{1,2}[y,\bar{x}]dy \\ +O(f^{(3)}(\bar{x})) \ . \tag{B10}$$

This expression can be simplified considerably using the following relations:

$$\frac{\partial}{\partial y}\chi_{1,2}[y,\bar{x}]=-\frac{\alpha_{1,0}^2(\bar{x})}{2}\frac{\alpha_{2,0}(y)}{\alpha_{1,0}^3(y)} \tag{B11}$$

and

$$\chi_{1,2}(\bar{x},\bar{x})=0 \tag{B12}$$

which are a consequence of Eqs. (41a) and (47a), respectively. Instead of Eq. (B10) one obtains

$$\chi_2[x_0,\bar{x}]=\frac{1}{2!}(\chi_{1,2}[x_0,\bar{x}])^2f^{(4)}(\bar{x}) \\ +O(f^{(3)}(\bar{x})) \ . \tag{B13}$$

A general proof for χ_l ($l>2$) is simply given by induction repeating the arguments used above. Therefore we arrive at the general relationship

$$\chi_l[x_0,\bar{x}]=\frac{1}{l!}(\chi_{1,2}[x_0,\bar{x}])^lf^{(2l)}(\bar{x}) \\ +O(f^{(2l-1)}(\bar{x})) \tag{B14}$$

which proves, in connection with Eq. (13), both Eqs. (45) and (47c).

[1]P. Hänggi and H. Thomas, Phys. Rep. 88, 207 (1982).
[2]G. Haag and P. Hänggi, Z. Phys. B 34, 411 (1979); 39, 269 (1980).
[3]G. Haag, W. Weidlich, and P. Alber, Z. Phys. B 26, 297 (1977); 30, 345 (1978).
[4]R. Zwanzig, K. S. J. Nordholm, and W. C. Mitchell, Phys. Rev. A 5, 2680 (1972).
[5]H. Mori and H. Fujisaka, Prog. Theor. Phys. 49, 764 (1972).
[6]H. Grabert and W. Weidlich, Phys. Rev. A 21, 2147 (1980).
[7]N. G. van Kampen, Can. J. Phys. 39, 551 (1961).
[8]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[9]R. Kubo, K. Matsuo, and K. Kitahara, J. Stat. Phys. 9, 51 (1973).
[10]C. T. J. Alkemade, Physica (Utrecht) 24, 1029 (1958).
[11]N. G. van Kampen, Physica (Utrecht) 26, 585 (1960).
[12]N. G. van Kampen, Adv. Chem. Phys. 34, 245 (1976). As van Kampen has pointed out to us, Kubo *et al.* (Ref. 9) and van Kampen (Ref. 17) have obtained the same expression for Φ_1, Eq. (41b), not including $\alpha_{1,1}$.
[13]N. G. van Kampen, in *Thermodynamics and Kinetics of Biological Processes,* edited by A. I. Zotin (de Gruyter, Berlin, 1981).
[14]O. J. Eder, B. Kunsch, and T. Lackner, J. Chem. Phys. 72, 4667 (1980).
[15]O. J. Eder and T. Lackner, J. Chem. Phys. 76, 4637 (1982).
[16]J. E. Moyal, J. R. Stat. Soc. B 11, 150 (1949).
[17]N. G. van Kampen, J. Math. Phys. 2, 597 (1961).