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## Steady state fluctuations and the structure factor of a two-step chemical reaction

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**Abstract.** The non-linear Fokker-Planck equation is used to study the non-equilibrium concentration of a two-step chemical reaction. The non-linearities are systematically approximated and the concentration time correlation function is calculated analytically for two reaction schemes, with and without detailed balance, respectively. The corresponding structure factors are also calculated and it is found that they exhibit the same basic Lorentzian structure. The relation of our results to other work is also mentioned.

### 1. Introduction

Renewed interest in the characterisation of non-equilibrium steady states (NESS) and the behaviour of fluctuations about them has increased recently, especially in connection with the description of systems such as fluids supporting flows [1, 2] or chemical reactions [3-5].

Owing to the great diversity of properties that a NESS may exhibit, its proper description is far more difficult than for an equilibrium state. However, for the special case of NESS obeying the detailed balance (DB) condition, a number of thermodynamic properties usually connected with equilibrium or near-equilibrium states may also be applied. The property of detailed balance reflects on a macroscopic level the time reversal invariance of the microscopic equations of motion and it may be expressed in a variety of equivalent forms [6-8]. Here, we only consider systems whose stochastic dynamics may be described by the non-linear Fokker-Planck equation (NFPE), namely

$$\frac{\partial P(q, t)}{\partial t} = - \frac{\partial}{\partial q_i} K_i(q) P(q, t) + \frac{\partial^2}{\partial q_i \partial q_j} D_{ij}(q) P(q, t) \quad (1.1)$$

where  $q$  stands for a set of stochastic variables.

For a process described by this equation DB is expressed by the symmetry relations

$$P^0(q) = P^0(\tilde{q}) \quad (1.2a)$$

$$P(q, t; q^0) P^0(q^0) = P(\tilde{q}^0, t; \tilde{q}) P^0(\tilde{q}) \quad (1.2b)$$

where  $P(q, t; q^0)$  is the conditional probability density of the variables  $q$ , which for convenience are separated into even and odd ones  $q^\nu \rightarrow \tilde{q}^\nu \equiv \epsilon^\nu q^\nu$  with  $\epsilon^\nu = +1, -1$ , respectively, with respect to time reversal. The function  $P^0(q)$  is the time-independent

solution of equation (1.1) and it is assumed to be unique. When  $\text{DB}$  holds, the stationary solution of equation (1.1) may be found and used to define a generalised thermodynamic potential which allows one to assess the stability conditions on the solution.

On the other hand, for many non-equilibrium states the absence of  $\text{DB}$  is a typical non-linear effect. For instance, the non-linearities in equation (1.1) frequently induce non-linear couplings among the variables  $\{q\}$ , which in turn may lead to the breakdown of  $\text{DB}$  [9, 10]. Since, as indicated in equation (1.2),  $\text{DB}$  involves the full conditional probability density, it is to be expected that the non-equilibrium properties of the system will be affected by the presence or absence of  $\text{DB}$ . The purpose of this paper is twofold: firstly, to calculate analytically the concentration–correlation function and the corresponding structure factor for a two-step chemical reaction describable by equation (1.1). Secondly, to investigate how the presence or absence of  $\text{DB}$  affects the features of this measurable property of the reacting system. We find that, within our approximations of the non-linearities of the  $\text{NFPE}$ , the basic and rather simple structure of the spectra is not modified by the presence or absence of  $\text{DB}$ ; in both cases the spectrum is a simple Lorentzian.

To this end, in the next section we calculate analytically the steady state concentration correlation function for both the reversible and irreversible chemical reaction schemes. This is accomplished by systematically truncating the hierarchy of moments of the conditional probability up to second-order cumulants. The validity of the approximations involved in this procedure is assessed by calculating the same quantities numerically. Then in § 3 we obtain the corresponding spectral densities and the structure factors.

## 2. The concentration correlation function

### 2.1. The irreversible case

Consider the following chemical reaction scheme which does not obey detailed balance [11],



We assume that the amount of  $A$  is kept constant by appropriate feeding of the reactor and that  $E$  is eliminated instantaneously. The corresponding macroscopic rate equation is

$$dx(t)/dt = k_1 a - 2k_2 x^2(t) \quad (2.2)$$

where we have introduced the concentrations  $x = X/V$  and  $a = A/V$ , associated with species  $X$  and  $A$ , respectively, and  $V$  is the volume where the reaction takes place. Equation (2.1) generates the single steady state

$$x_s = (k_1 a / 2k_2)^{1/2}. \quad (2.3)$$

It has been shown by Horsthemke and Brenig [12] that the above two-step chemical reaction may be described from a stochastic point of view by the following  $\text{NFPE}$ :

$$\frac{\partial P(x, t)}{\partial t} = -\frac{\partial}{\partial x} [K(x)P(x, t)] + \frac{\partial^2}{\partial x^2} [D(x)P(x, t)]. \quad (2.4)$$

Here  $x$  denotes the fluctuating concentration and the drift and diffusion coefficients are given, respectively, by

$$K(x) = k_1 a + 2k_2 x / V - 2k_2 x^2 \quad (2.5a)$$

$$D(x) = (k_1 a + 4k_2 x^2) / 2V. \quad (2.5b)$$

At this point it is worth emphasising that, although the DB condition may be expressed in a variety of equivalent forms, for a multivariate NFPE it may be stated as a relation between the drift and diffusion coefficients, namely [9]

$$K_i(q) = -\frac{1}{P^0(q)} \frac{\partial}{\partial q_j} [D_{ij}(q) P^0(q)] \quad (2.6)$$

where  $P^0(q)$  stands for the equilibrium distribution function and the  $q$  represents the set of stochastic variables. It is easy to verify that equation (2.4) does not fulfil condition (2.6) and therefore it does not obey DB.

The stationary solution of equation (2.4) is given by [2]

$$P^{st}(x) = \phi(x) \exp[-Vx + \frac{3}{2}\sqrt{2} Vx_s \tan^{-1}(\sqrt{2}x/x_s)] \quad (2.7)$$

with

$$\phi(x) = N(1 + 2x^2/x_s^2)^{1/2} \quad (2.8)$$

where  $x_s$  is given by equation (2.3) and  $N$  is a normalisation constant.

As mentioned in the introduction, we are interested in evaluating the concentration correlation function for the stationary state defined by equation (2.7). This correlation function is defined in general as

$$C(t) = \langle x_0 \langle x(t) \rangle_{x_0/st} \rangle_{x_0/st} - \langle x_0 \rangle_{st} \langle \langle x(t) \rangle_{x_0/st} \rangle_{x_0/st} \quad (2.9)$$

where  $x_0 = x(0)$  is the initial concentration value. Here the notation indicates the following: take a certain  $x_0$ , calculate the average value  $\langle x(t) \rangle$  conditional on the given  $x_0$ ; then multiply this conditional average by  $x_0$  and average over the values of  $x_0$  as they occur in the state under consideration. Thus, the main task is to calculate the conditional average. For this purpose from equations (2.4) and (2.5) we obtain the following coupled set of equations for the first three conditional moments of  $P(x, t)$ †

$$d\langle x \rangle / dt = k_1 a + (2k_2 / V) \langle x \rangle - 2k_2 \langle x^2 \rangle \quad (2.10)$$

$$d\langle x^2 \rangle / dt = (k_1 / V) a + 2k_1 a \langle x \rangle + 8(k_2 / V) \langle x \rangle - 4k_2 \langle x^3 \rangle \quad (2.11)$$

$$d\langle x^3 \rangle / dt = 3(k_1 / V) a \langle x \rangle + 3k_1 a \langle x^2 \rangle + 18(k_2 / V) \langle x^3 \rangle - 6k_2 \langle x^4 \rangle. \quad (2.12)$$

The first two equations may be decoupled by expanding  $\langle x^3 \rangle$  in a Taylor series around  $\langle x \rangle$ :

$$\langle x^3 \rangle = \langle x \rangle^3 + 3\langle (x - \langle x \rangle)^2 \rangle \langle x \rangle + \langle (x - \langle x \rangle)^3 \rangle \quad (2.13)$$

and then neglecting the last term since it can be systematically shown always to be of higher order than the first two [13]. Furthermore, if we also take the thermodynamic limit, the equations for the first two moments of  $P(x, t)$  become

$$d\langle x \rangle / dt = k_1 a - 2k_2 \langle x^2 \rangle \quad (2.14)$$

$$d\langle x^2 \rangle / dt = 2k_1 a \langle x \rangle - 12k_2 \langle x \rangle \langle x^2 \rangle + 8k_2 \langle x \rangle^3. \quad (2.15)$$

† For simplicity of notation, from here on we omit the subscript  $x_0$  in the conditional moments.

According to equation (2.9),  $C(t)$  will be finite if  $\langle x(t) \rangle$  is finite as well and this, in turn, implies that the solution to the above set of equations should be stable. It can be shown that the singular points associated with equations (2.14) and (2.15) in the space spanned by  $\langle x \rangle$  and  $\langle x^2 \rangle$  are a stable nodal point  $Q_1(x_s, x_s^2)$ , a saddle point  $Q_2(0, x_s^2)$  and an unstable nodal point  $Q_3(-x_s, x_s^2)$ . Therefore, in the neighbourhood of  $Q_1$  the solutions of the above equations are stable. Then a small alteration of the initial value  $x_0$  changes their value to a different one that remains in the vicinity of the original value. Hence the fluctuations in  $x$  are expected to be small and finite around  $Q_1$  and  $C(t)$  is well defined for any value of the positive parameters  $k_1, k_2$  and  $a$ . On the other hand, in the neighbourhood of  $Q_2, Q_3$ , a continually acting perturbation will have a cumulative effect, resulting in a continuous drift of the solution from one value to another. In this paper we approximate the above equations for the moments only in the vicinity of  $Q_1$ . Hence equations (2.11) and (2.12) may be rewritten as the single second-order equation

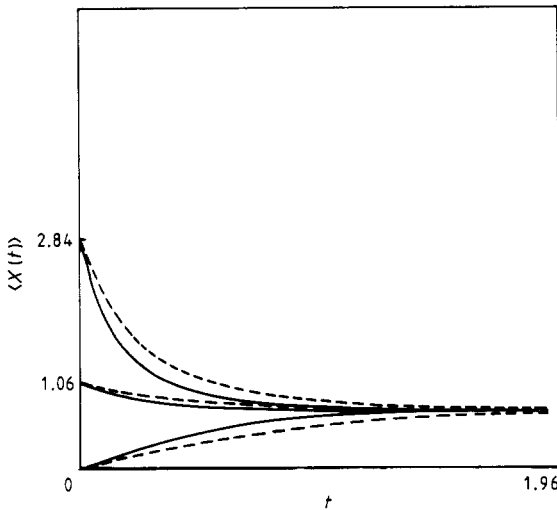
$$(1/2k_2) d^2\langle x \rangle / dt^2 + 6\langle x \rangle d\langle x \rangle / dt = 4k_1 a \langle x \rangle - 8k_2 \langle x \rangle^3. \tag{2.16}$$

Although it is difficult to solve this equation analytically owing to its non-linear character, we can always obtain an exact numerical solution; in figure 1 we have plotted the fourth-order Runge-Kutta solution for  $k_1 = 1, k_2 = 1$  and  $a = 1$  with different initial conditions. However, some insight into the behaviour of its solution may be gained by considering the special case when  $k_2 \gg 1$ . Under this approximation equation (2.16) reduces to

$$d\langle x \rangle / dt = \frac{2}{3}k_1 a - \frac{4}{3}k_2 \langle x \rangle^2 \tag{2.17}$$

whose solution is

$$\langle x(t) \rangle = x_s(1 + \delta e^{-\alpha t}) / (1 - \delta e^{-\alpha t}) \tag{2.18}$$



**Figure 1.** The fourth-order Runge-Kutta solution (—) of equation (2.14) and (2.15) as a function of time, when  $k_1 = 1, k_2 = 1$  and  $a = 1$ . Each curve corresponds to different initial conditions. The broken lines represent the analytical overdamped solution of equation (2.16) for the same initial conditions as before.

where  $x_s$  is given by equation (2.3) and

$$\delta = (x_0 - x_s)/(x_s + x_0) \quad (2.19a)$$

$$\alpha = \frac{4}{3}(2k_1 k_2 a)^{1/2}. \quad (2.19b)$$

Notice that  $0 < \delta < 1$  and that as  $t \rightarrow \infty$ ,  $\langle x(t) \rangle$  reduces to  $x_s$ . Also, if  $t \rightarrow 0$ ,  $\langle x(t) \rangle \rightarrow x_0$  as expected.

The approximate analytic solution (2.18) is very close to the numerical one for all times and become asymptotically identical; in figure 1 we have also plotted this overdamped solution for the same parameters and initial conditions as before. It must be remarked that this analytical approximation is good for 'large times' even when  $k_2 = 1$ .

Using equations (2.18) and (2.19) we find that the concentration correlation function in the stationary state is given by

$$C^{st}(t) = \langle x_0 x_s (1 + \delta e^{-\alpha t}) / (1 - \delta e^{-\alpha t}) \rangle_{st} - (x_0 + 1/8V) \langle x_s (1 + \delta e^{-\alpha t}) / (1 - \delta e^{-\alpha t}) \rangle_{st}. \quad (2.20)$$

Now, since the stationary average of an arbitrary function  $x$  may be calculated from equation (A6), after some tedious but straightforward algebra we arrive at

$$C^{st}(t) = \frac{3}{4}[(x_s/V) \exp(-\alpha t)] + O(1/V^2). \quad (2.21)$$

It is worth emphasising that the distribution of the initial values  $x_0$  appearing in equation (2.20) is, in principle, completely arbitrary. For instance, if initially there were exactly  $x_0$  molecules of  $x$ , all the quantities in the last equation are just numbers. However, due to inaccuracies in weighting, etc, one obtains a distribution about some initial concentration which in general would be Gaussian. For large systems this distribution can be conveniently approximated by a binomial distribution:

$$\text{prob}\{x(0) = r\} = \binom{n}{r} p^r (1-p)^{n-r} \quad r = 0, 1, 2, \dots, n \quad (2.22)$$

with mean  $m$  and variance  $\sigma$  given by

$$m = np \quad \sigma = np(1-p) \quad (2.23)$$

where  $p$  is the probability for success of a single event.

To study the effect of varying  $p$  for fixed  $x_0$ , i.e. the effect of various degrees of inaccuracy of the determination of the initial conditions, we may adjust  $n$  simultaneously with  $p$  so that the product  $np = x$  is constant. In this form as  $p$  approaches unity the initial conditions are better determined and the coefficients in equation (2.21) are numbers depending on the initial value  $x_0$ . From the concentration correlation (2.21) we can derive the corresponding spectral density and the structure factor as will be shown in § 3.

## 2.2. The reversible case

We now consider the following reversible reaction system



where  $A$  and  $E$  are kept constant by suitable reservoirs and  $k_1'$  and  $k_2'$  stand for the backward reaction constants. The macroscopic rate equation is now

$$dx(t)/dt = k_1 a - k_1' x(t) - 2k_2 x^2(t) + 2k_2' e \quad (2.25)$$

where  $e = E/V$  is the concentration associated with species  $E$ . The stationary solution of this equation is

$$x_s = (1/4k_2)[-k'_1 + (k_1'^2 + 8k_1k_2a + 16k_2k'_2e)^{1/2}] \tag{2.26}$$

where we have chosen the positive solution since the concentration should always be positive. Following the prescription given by Horsthemke and Brenig [12] to construct the NFPE associated with (2.24), we find that the drift and diffusion coefficients are, respectively,

$$k(x) = k_1a + 2k'_2e + (2k_2x/V) - k'_1x - 2k_2x^2 \tag{2.27}$$

$$D(x) = (k_1a + 4k'_2e + k'_1x + 4k_2x^2)/4V. \tag{2.28}$$

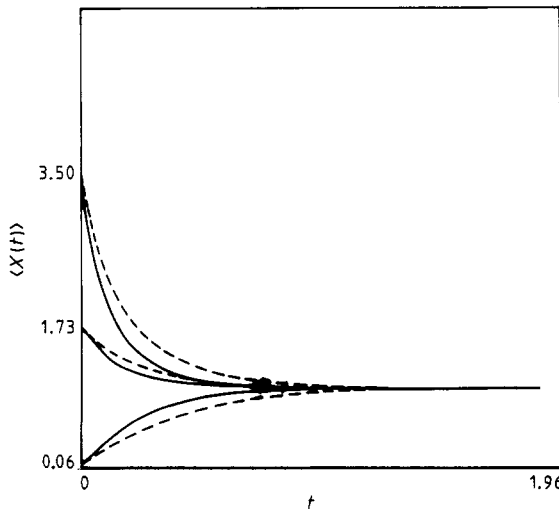
We can show that, indeed, these coefficients satisfy the detailed balance condition (2.6), which is the mesoscopic expression of the reversibility of scheme (2.24).

As before, from the corresponding NFPE we can obtain a coupled system of equations for the successive moments of the distribution function  $P(x, t)$ . Again this set of equations may be decoupled by using the same approximation (2.13) and by taking the thermodynamic limit. This leads to

$$d\langle x \rangle / dt = k_1a + 2k'_2e - k'_1\langle x \rangle - 2k_2\langle x \rangle \tag{2.29a}$$

$$d\langle x^2 \rangle / dt = (2k_1a + 4k'_1e)\langle x \rangle - 2k'_1\langle x^2 \rangle - 12k_2\langle x \rangle\langle x^2 \rangle + 8k_2\langle x \rangle^3. \tag{2.29b}$$

As in the irreversible scheme, it can be shown that the singular points associated with equations (2.29) in the space spanned by  $\langle x \rangle$  and  $\langle x^2 \rangle$  are a stable nodal point, a saddle point and an unstable nodal point. Our analysis would be limited to the stable point since it is the only one accessible from the physical point of view. In figure 2 we show the fourth-order Runge-Kutta solution of system (2.29) for  $k_1 = 1, k_2 = 1, k'_1 = 1, k'_2 = 1, a = 1$  and  $e = 1$ , and for several initial conditions.



**Figure 2.** The fourth-order Runge-Kutta solution (—) of equations (2.29) as a function of time, when  $k_1 = 1, k_2 = 1, k'_1 = 1, k'_2 = 1, a = 1$  and  $e = 1$ . Each curve corresponds to different initial conditions. (- -) refers to the analytical overdamped solution of equation (2.30) for the same initial conditions as before.

For the purpose of obtaining an approximate analytic solution we rewrite these equations as

$$\frac{1}{2k_2} \frac{d^2\langle x \rangle}{dt^2} + \frac{3}{2} \frac{k_1'}{k_2} \frac{d\langle x \rangle}{dt} + 6\langle x \rangle \frac{d\langle x \rangle}{dt} = \frac{k_1'}{k_2} (ak_1 + 2ek_2') + (4k_1a + 8k_2'e - k_1'^2/k_2)\langle x \rangle - 6k_1'\langle x \rangle^2 - 8k_2\langle x \rangle^3 \quad (2.30)$$

and, as in § 2.1, we consider the case where  $k_2$  is large but assuming that  $k_2'$  is also large. Thus, for a given initial value  $x = \langle x(0) \rangle$  the general solution of the resulting approximate equation is

$$\langle x(t) \rangle = \frac{x_s - \varepsilon x_s^- \exp(-\beta t)}{1 - \varepsilon \exp(-\beta t)} \quad (2.31)$$

where now  $x_s$  is given by equation (2.26) and

$$x_s^- = (1/4k_2)[-k_1' - (k_1'^2 + 8k_1k_2a + 16k_2k_2'e)^{1/2}] \quad (2.32a)$$

$$\varepsilon = (x_s - x_0)/(x_s^- - x_0) \quad (2.32b)$$

$$\beta = \frac{4}{3}k_2(x_s - x_s^-). \quad (2.32c)$$

The approximate analytic solution (2.31) is very close to the numerical one for all times and become asymptotically identical; in figure 2 we have plotted them for the same values of the parameters and for the same initial conditions. As in the irreversible case, it must be pointed out that the overdamped solution is also fairly good when  $k_2 = k_1' = 1$  and the time is 'long enough'.

Following the same procedure that led us to equation (2.19), we obtain a concentration correlation function with exactly the same structure as (2.19), but with a  $x_s$  given by equation (2.26) instead of (2.3). Then, from equation (A7) we explicitly obtain

$$C^{\text{st}}(t) = (\lambda_1/4V) \exp(-\beta t) + O(1/V^2) \quad (2.33)$$

where  $\lambda_1$  is a constant (see equation (A8a)).

### 3. The structure factor

From the concentration correlation expressions of the previous section, we now derive the corresponding spectral densities. The latter are obtained from the former through the Wiener-Khinchine theorem [14]

$$S(\omega) = \frac{1}{\pi} \int_0^\infty c(t) \cos \omega t \, dt. \quad (3.1)$$

Using equations (2.21) and (2.33)

$$S(\omega) = \frac{C^{\text{st}}}{\pi} \frac{\gamma}{\gamma^2 + \omega^2} \quad (3.2)$$

where

$$C^{\text{st}} = \frac{3}{4}x_s/V \quad \text{and} \quad \gamma = \alpha \quad (3.3)$$



for the irreversible case, and where

$$C^{st} = \lambda_1/2V \quad \text{and} \quad \gamma = \beta \quad (3.4)$$

for the reversible one.

Clearly the structure of both spectra is the same but the amplitude and width of the Lorentzians are different. It should also be mentioned that this result of a Lorentzian contribution to the spectrum is in agreement with the results of Bloomfield and Benbasat [15] obtained using a different approach.

#### 4. Concluding remarks

A two-step chemical reaction has been studied by means of a NFPE. The method used to calculate the steady state concentration fluctuations is based on the stability properties of the singular points for the system of equations for the first moments. An important feature of the method is that the approximations involved in the truncation of the hierarchy of equations for the moments are systematic. That is, they may be shown to be equivalent to an expansion in terms of a small parameter of the system [13].

The analysis of the preceding sections also showed that for both the reversible and irreversible reaction schemes, the fluctuations spectra are Lorentzian; a result which is not obvious *a priori*. This result clearly suggests that the influence of detailed balance on the structure of the spectra is negligible within the approximations used. This lack of influence may be due to different reasons: for instance, to the thermodynamic limit approximation used which has the effect of scaling down the amplitude of the fluctuations. It may also be a consequence of the truncation of the hierarchy of moments of  $P(x, t)$ , introduced in § 2 in order to make the problem tractable. Since, as indicated in equation (1.1), detailed balance involves the full distribution function, the truncation has the effect of approximating  $P(x, t)$  by its lower order moments only. This in turn eliminates many of the non-linear features of the system and, presumably, also the influence of detailed balance. This indicates the necessity of better approximations of the NFPE.

It is worth pointing out that similar conclusions concerning the lack of influence of detailed balance on a macroscopic measurable property of a fluid have been obtained from a kinetic analysis based on the Boltzmann equation [16].

#### Acknowledgments

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#### Appendix

In this appendix we calculate the correlation function  $C(t)$ , equation (2.9), of the reduced concentration  $x$ ,

$$C(t) = \langle x_0 \langle x(t) \rangle_{x_0} \rangle_{st} - \langle x_0 \rangle_{st} \langle \langle x(t) \rangle_{x_0} \rangle_{st}.$$

We treat the reversible scheme only and, at the end, we obtain the irreversible one as a particular case. We proceed in two steps: firstly we derive an approximate expression

for the stationary mean value of an arbitrary function of the reduced concentration and, secondly, we apply this expression to equation (2.9) with the solution (2.31).

Let  $\psi(x)$  be an arbitrary, but rather regular, function of the reduced concentration  $x$ . Its stationary mean value is defined as

$$\langle \psi(x) \rangle = \int_0^\infty \psi(x) P^{\text{st}}(x) dx. \quad (\text{A1})$$

The stationary solution of equation (2.4) is given by

$$P^{\text{st}}(x) = \frac{N}{D(x)} \exp\left(\int \frac{K(x)}{D(x)} dx\right). \quad (\text{A2})$$

Using expressions (2.27) and (2.28) and after a straightforward, but very tedious, integration one finds the following explicit expression for the stationary probability density:

$$P^{\text{st}}(x) = \phi(x) \exp(Vf(x)) \quad (\text{A3})$$

where

$$f(x) = -x + \frac{B_3}{4k_2 B_2} \tan^{-1}(B_1/B_2) - \frac{k'_1}{8k_2} \ln(2VD(x)) \quad (\text{A4})$$

and

$$\phi(x) = \frac{N}{D^{1/2}(x)} \exp\left(-\frac{k'_1}{B_2} \tan^{-1}(B_1/B_2)\right). \quad (\text{A5})$$

Here  $D(x)$  is the diffusion coefficient (equation (2.28)),  $N$  is the normalisation constant and  $B_1$ ,  $B_2$  and  $B_3$  are given by

$$B_1 = k'_1 + 8k_2x \quad (\text{A6a})$$

$$B_2 = (16k_1k_2a + 64k_2k'_2e - k_1'^2)^{1/2} \quad (\text{A6b})$$

$$B_3 = k_1'^2 + 24k_1k_2a + 64k_2k'_2e. \quad (\text{A6c})$$

It is not very difficult to show that the stationary reduced concentration  $x_s$ , equation (2.26), is a saddle point of  $f(x)$ . Then, we can use the method of steepest descent [17, 18] to solve (A1) up to order  $1/V$ , obtaining

$$\langle \psi(x) \rangle = \psi(x_s) + (1/4V)[\lambda_1\psi''(x_s) + \lambda_2\psi'(x_s)] + O(1/V^2) \quad (\text{A7})$$

where

$$\lambda_1 = -2/f'(x_s) \quad (\text{A8a})$$

$$\lambda_2 = -\frac{4}{f''(x_s)} \frac{\phi'(x)}{\phi(x)} + 2 \frac{f'''(x_s)}{(f''(x_s))}. \quad (\text{A8b})$$

Applying formula (A6) we find the stationary mean value of the reduced concentration  $x$

$$\langle x \rangle = x_s + \lambda_2/4V \quad (\text{A9})$$

the stationary correlation function

$$C = \langle x^2 \rangle - \langle x \rangle^2 = \lambda_1/2V \quad (\text{A10})$$

and, using the solution (2.31), the time-dependent correlation function

$$C(t) = (\lambda_1/2V) \exp(-\beta t) \quad (\text{A11})$$

where  $\beta$  is given by (2.32).

We remark that, although  $\lambda_1$  and  $\lambda_2$  are constants, their explicit expressions are, in the general case, very cumbersome. However, in the irreversible scheme, which is obtained by taking  $k'_1 = 0$ ,  $k'_2 = 0$  and  $e = 0$ , one finds

$$\lambda_1 = \frac{3}{2}x_s \quad \text{and} \quad \lambda_2 = \frac{1}{2}. \quad (\text{A12})$$

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