

FLUCTUATIONS IN REVERSIBLE CHEMICAL REACTIONS*

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The paper proposes a new approach to describe fluctuations of reversible chemical reactions in closed systems. The deterministic rate laws are cast into the form of nonlinear Onsager type transport laws. By means of nonlinear transport theory a Fokker–Planck equation describing the stochastic process of concentration fluctuations is obtained. It is shown that the stochastic formulation reduces to the correct deterministic rate laws in the thermodynamic limit $V \rightarrow \infty$ with the concentrations kept fixed. Concrete examples of reactions in ideal mixtures are given and the results of the presented approach are compared with those of the usual approach by means of a birth and death type master equation. It is shown that both approaches lead to the same stationary probability and exhibit the same natural boundaries reflecting the fact of a restricted state space. The proposed Fokker–Planck equation is different from the Fokker–Planck equation obtained from the master equation by truncating its Kramers–Moyal expansion. However, the two equations are shown to have identical Fokker–Planck coefficients in the vicinity of the deterministic equilibrium state. Compared with the usual master equation approach the proposed stochastic modeling of chemical reactions has the advantage of allowing for a straightforward extension to reactions in non-ideal mixtures.

1. Introduction

On a deterministic level, chemical reactions are described by rate laws whose validity is well established, at least for reactions in dilute gases where they have the form of simple power laws¹). On a more refined level, which includes fluctuations of the particle concentrations, the reaction is described in terms of a stochastic process. The problem of the mutual connection between the deterministic and the stochastic levels of description arises quite generally in the theory of many-body systems. For systems in the linear regime near equilibrium

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the Onsager theory gives a rather complete answer to this question. However, for chemical reactions linear transport theory provides only a poor approximation²).

Recently, an extension of Onsager's theory to nonlinear systems has been obtained on the basis of statistical mechanical considerations³). In this approach fluctuations are described by a "nonlinear" Fokker-Planck equation characterized by a thermodynamic potential and a transport matrix. Since this theory starts out from a molecular description in terms of continuous phase functions⁴), it does not strictly apply to chemical reactions where the particle numbers vary in a discrete state space⁵). However, for large homogeneous systems the discreteness should be of minor importance and we expect that valuable results can be obtained from a Fokker-Planck description.

In order to see whether such an approach by nonlinear transport theory is appropriate for chemical reactions, we examine elementary reactions in ideal mixtures where a comparison with the master equation approach of the birth-and-death type is possible⁶).

The main results of the paper can be summarized in the following points:

a) The proposed stochastic description of chemical reactions reduces to the correct deterministic behavior in the limit of a large volume V with the concentrations kept fixed.

b) For reactions in ideal mixtures the newly proposed Fokker-Planck equation has (apart from a continuum approximation by means of Stirling's formula) the same stationary probability as the associated birth-and-death type master equation. Further, the master equation and the Fokker-Planck equation have the same natural boundaries. The nonlinear Fokker-Planck equation also exhibits the multiplicative noise structure inherent in the master equation.

c) The truncated Kramers-Moyal expansion of the master equation leads to a different Fokker-Planck equation with an approximate stationary probability only, and the character of the restricted state space is not preserved by the truncation since the resulting Fokker-Planck equation has no natural boundaries.

d) On the other hand, the two Fokker-Planck equations coincide near equilibrium since the two drift expressions differ only by terms of higher order in $1/V$, and the state-dependent diffusion coefficients have the same values and the same slopes at the deterministic equilibrium state.

e) The approach naturally extends to nonideal mixtures where the usual approach by birth and death type master equations fails.

We want to point out that the present approach copes with the description of local concentration fluctuations as well. The theory should be particularly useful in situations where pressure and temperature fluctuations, and eventually convection, have to be taken into account⁷). Since the dynamics of the latter variables is governed by nonlinear transport laws of the same structure as those

proposed here for chemical reactions^{4,8}), most processes in chemical physics and hydromechanics and their mutual interactions can be treated in a unified manner.

The paper is organized as follows: section 2 studies the deterministic description of chemical reactions in ideal mixtures. The rate laws are cast into the form of Onsager type transport laws. The meaning of the free energy and the transport coefficients in these transport laws is clarified in section 3, where these quantities are shown to emerge naturally from a stochastic theory governed by a master equation of the birth and death type. Finally, section 4 addresses the problem of an approximate Fokker-Planck description of chemical reactions.

2. Transport equations for chemical reactions in ideal mixtures

In this section we consider mixtures of ideal gases or ideal liquid mixtures where some of the components undergo chemical reactions. We assume that the system is confined to a constant volume V and that it is closed with respect to particle exchange. An external heat bath is supposed to maintain a constant temperature T . In particular we restrict ourselves to situations where the chemical reactions are so slow that the system is always in mechanical equilibrium and homogeneous.

The appropriate thermodynamic potential to describe isothermal and isochore systems is the Helmholtz free energy A which for an ideal homogeneous system may be written⁹)

$$A = A_0 + \sum_{i=1}^n N_i(\varphi_i + k_B T \ln N_i), \quad (2.1)$$

where A_0 is the free energy of the nonreacting components (e.g. the solvent). The n reacting components have particle numbers N_i , and k_B is the Boltzmann constant. A_0 and the coefficients φ_i are temperature dependent.

The chemical potential (per particle) of the i -component is given by

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_j} = \mu_i^0 + k_B T \ln N_i, \quad (2.2)$$

where

$$\mu_i^0 = \varphi_i + k_B T. \quad (2.3)$$

The n components undergo r reversible chemical reactions characterized by the stoichiometric equations

$$\sum_{i=1}^n \nu_i^\alpha X_i = 0 \quad (\alpha = 1, \dots, r), \quad (2.4)$$

where X_i denotes the chemical symbol of the i -component, and the ν_i^α 's are the stoichiometric numbers which are positive for reaction products and negative for reactants.

Due to the chemical reactions the particle number N_i change in time according to

$$\dot{N}_i = \sum_{\alpha=1}^r \nu_i^\alpha \dot{\lambda}_\alpha, \quad (2.5)$$

where λ_α is the progress variable for the α -reaction.

Since the chemical reactions are the only processes leading to a change of the particle numbers, the N_i 's are not all independent for $r < n$, but rather can be specified in terms of their initial values N_i^0 and the progress variables

$$N_i = N_i^0 + \sum_{\alpha=1}^r \nu_i^\alpha (\lambda_\alpha - \lambda_\alpha^0). \quad (2.6)$$

In this case, which we will consider in the following for the sake of concreteness, the r progress variables λ_α are the independent variables corresponding to the r degrees of freedom of the system. As a consequence, the free energy A can be expressed as a function of the progress variables only. Then, the time rate of change of the free energy reads

$$\dot{A} = - \sum_{\alpha=1}^r \chi_\alpha \dot{\lambda}_\alpha, \quad (2.7)$$

where

$$\chi_\alpha = - \left(\frac{\partial A}{\partial \lambda_\alpha} \right)_{T, V, \lambda_\beta} \quad (2.8)$$

is the chemical affinity of the α -reaction. The χ_α 's can be looked upon as the thermodynamic forces driving the system towards equilibrium where the free energy attains a minimum. The time rate of change of A can also be written

$$\dot{A} = \sum_{i=1}^n \mu_i \dot{N}_i, \quad (2.9)$$

which yields with (2.2), (2.5) and (2.7) an expression for the affinities

$$\chi_\alpha = - \sum_{i=1}^n \nu_i^\alpha \mu_i = - \sum_{i=1}^n \nu_i^\alpha (\mu_i^0 + k_B T \ln N_i). \quad (2.10)$$

In thermal equilibrium we have $\chi_\alpha = 0$, and consequently

$$\sum_{i=1}^n \nu_i^\alpha \mu_i^0 = -k_B T \sum_{i=1}^n \nu_i^\alpha \ln \bar{N}_i, \quad (2.11)$$

where the \bar{N}_i 's denote the equilibrium particle numbers. In terms of the

equilibrium constants

$$K_\alpha = \exp\left(-\frac{1}{k_B T} \sum_{i=1}^n \nu_i^\alpha \mu_i^0\right) \quad (2.12)$$

the condition for equilibrium reads

$$\prod_{i=1}^n \bar{N}_i^{\nu_i^\alpha} = K_\alpha \quad (\alpha = 1, \dots, r). \quad (2.13)$$

Further, the affinities (2.10) are readily expressed as

$$\chi_\alpha = k_B T \ln \frac{K_\alpha}{\prod_{i=1}^n \bar{N}_i^{\nu_i^\alpha}}. \quad (2.14)$$

On a deterministic level of description the generally non-linear relaxation towards equilibrium is determined by the rate equations. We assume that the chemical reactions are elementary. Then, the time rate of change of the progress variables is given by

$$\dot{\lambda}_\alpha = V(k_\alpha \Pi_\alpha^+(c_i) - k'_\alpha \Pi_\alpha^-(c_i)), \quad (2.15)$$

and we have

$$\dot{c}_i = \sum_{\alpha=1}^r \nu_i^\alpha (k_\alpha \Pi_\alpha^+(c_j) - k'_\alpha \Pi_\alpha^-(c_j)), \quad (2.16)$$

where k_α and k'_α are the volume independent forward and backward rate constants, respectively. The c_i 's are the particle densities

$$c_i = \frac{N_i}{V} \quad (2.17)$$

and the symbols Π_α^+ , Π_α^- denote the products

$$\Pi_\alpha^+(c_i) = \prod_{i, \nu_i^\alpha > 0} c_i^{\nu_i^\alpha}, \quad (2.18)$$

$$\Pi_\alpha^-(c_i) = \prod_{i, \nu_i^\alpha < 0} c_i^{-\nu_i^\alpha}. \quad (2.19)$$

These are products of particle densities of the reaction products and the reactants, respectively.

Since the $\dot{\lambda}_\alpha$ vanish in equilibrium, we see on comparison with (2.13) that the rate constants are related by

$$\frac{k_\alpha}{k'_\alpha} = \frac{K_\alpha}{V^{\sigma^\alpha}} \equiv \bar{K}_\alpha, \quad (2.20)$$

where

$$\sigma^\alpha = \sum_{i=1}^n \nu_i^\alpha. \quad (2.21)$$

The relation (2.20) can be used to express the affinities (2.14) in terms of the particle concentrations

$$\chi_\alpha = k_B T \ln \frac{\bar{K}_\alpha}{\prod_{i=1}^n c_i^{\nu_i^\alpha}} \quad (2.22)$$

The deterministic rate equations may be cast into the form of nonlinear Onsager-type transport equations³⁾

$$\dot{\lambda}_\alpha = L^\alpha \chi_\alpha, \quad (2.23)$$

where the flows $\dot{\lambda}_\alpha$ are expressed in terms of the driving forces χ_α . The transport coefficients are given by

$$L^\alpha = \frac{V k'_\alpha \Pi_+^\alpha(c_i) - \bar{K}_\alpha \Pi_-^\alpha(c_i)}{k_B T \ln \Pi_+^\alpha(c_i) - \ln \bar{K}_\alpha \Pi_-^\alpha(c_i)} \quad (2.24)$$

These coefficients depend on the state of the system, and they are always positive since

$$\frac{x-y}{\ln x - \ln y} \geq 0, \quad \text{for } x, y \geq 0. \quad (2.25)$$

The L^α 's are well-behaved in the vicinity of the equilibrium state $c_i = \bar{c}_i$ ($\lambda_\alpha = \bar{\lambda}_\alpha$) where the numerator and the denominator of (2.24) vanish. To first order in the deviations from equilibrium we find

$$L^\alpha = \bar{L}^\alpha + \sum_{i=1}^n L_i^\alpha (c_i - \bar{c}_i), \quad (2.26)$$

$$L^\alpha = \bar{L}^\alpha + \sum_{\beta=1}^r L_\beta^\alpha (\lambda_\beta - \bar{\lambda}_\beta), \quad (2.27)$$

where

$$\bar{L}^\alpha = \frac{V}{k_B T} k'_\alpha \Pi_+^\alpha(\bar{c}_i) = \frac{V}{k_B T} k_\alpha \Pi_-^\alpha(\bar{c}_i) \quad (2.28)$$

is the equilibrium value of L^α , while

$$L_i^\alpha = \frac{1}{2} \bar{L}^\alpha \frac{|\nu_i^\alpha|}{\bar{c}_i} \quad (2.29)$$

and

$$L_\beta^\alpha = \frac{1}{2V} \bar{L}^\alpha \sum_{i=1}^n \frac{|\nu_i^\alpha| \nu_i^\beta}{\bar{c}_i} \quad (2.30)$$

give the slopes.

Using (2.5) and (2.10) the transport equations (2.23) may be written

$$\dot{N}_i = - \sum_{j=1}^n L^{ij} \left(\frac{\partial A}{\partial N_j} \right)_{T, V, N_k}, \quad (2.31)$$

where

$$L^{ij} = \sum_{\alpha=1}^r \nu_i^\alpha \nu_j^\alpha L^\alpha. \quad (2.32)$$

The form (2.31) of the transport equations can also be obtained for $r \geq n$.

The free energy (2.1) and the transport coefficients (2.24) are extensive quantities of the form

$$\begin{aligned} A &= Va(c_k, T), \\ L^{ij} &= Vl^{ij}(c_k, T), \end{aligned} \quad (2.33)$$

where a and l^{ij} are functions of the intensive variables c_k and T only. The deterministic law (2.31) may then be written

$$\dot{c}_i = - \sum_{j=1}^n l^{ij} \frac{\partial a}{\partial c_j}. \quad (2.34)$$

It might appear that these transport equations are just a complicated way of writing the "simple" rate laws (2.16). We shall demonstrate, however, in the following section that the free energy and the transport coefficients which appear in the transport equations (2.34) have a well-defined meaning within the stochastic theory of chemical reactions. They thus provide a convenient starting point for the investigation of fluctuations in chemical reactions.

3. Master equation approach and connection with transport equations

For chemical reactions in ideal mixtures there exists a well-known method for the formulation of the stochastic theory in terms of a birth-and-death master equation. Since this method has been clearly presented in several reviews and papers⁶⁾ we shall not repeat the physical and combinatorial arguments leading to such a description, but rather will discuss two specific reactions which will serve as examples to illustrate the connection between the master equation approach and the deterministic transport equations given in section 2.

3.1. Reversible unimolecular reaction

In a first example we investigate the simple isomerization reaction



These relations specify the rate constants and the stoichiometric numbers $\nu_1 = -\nu_2 = 1$. The deterministic rate law reads*

$$\dot{c}_1 = -\dot{c}_2 = kc_2 - k'c_1. \quad (3.2)$$

In this example the progress variable λ can be identified with the particle number $N_1 = \lambda$, and the linear dependence (2.6) between the particle numbers N_1 and N_2 has the form

$$N_1 + N_2 = N_1^0 + N_2^0 \equiv N \equiv Vc, \quad (3.3)$$

where N is a constant for closed systems. The equilibrium condition (2.13), (2.20) reads

$$\frac{\bar{N}_1}{\bar{N}_2} = \frac{\bar{N}_1}{N - \bar{N}_1} = \frac{k}{k'} = K = \bar{K}, \quad (3.4)$$

where K denotes the equilibrium constant.

For a closed system the master equation associated with the isomerization reaction (3.1) reads^{6b)}

$$\begin{aligned} \dot{p}_i(N_i) = & k(N - N_i + 1)p_i(N_i - 1) + k'(N_i + 1)p_i(N_i + 1) \\ & - k(N - N_i)p_i(N_i) - k'N_i p_i(N_i), \end{aligned} \quad (3.5)$$

which may also be written

$$\dot{p}_i(N_i) = \sum_{N_i'} \{W(N_i' \rightarrow N_i)p_i(N_i') - W(N_i \rightarrow N_i')p_i(N_i)\}, \quad (3.6)$$

where the transition probability $W(N_i \rightarrow N_i')$ scales with the volume V as

$$W(N_i \rightarrow N_i') = Vw(c_i, N_i' - N_i), \quad (3.7)$$

where

$$w(c_i, \Delta) = k(c - c_i)\delta_{\Delta,1} + k'c_i\delta_{\Delta,-1}. \quad (3.8)$$

This form of the transition probability leads to natural boundaries at $N_i = 0$ and $N_i = N$.

The stationary probability of (3.5) is given by

$$p_{st}(N_i) = \frac{1}{Z'} \frac{\bar{N}_1^{N_i} (N - \bar{N}_1)^{N - N_i}}{N_i! (N - N_i)!}, \quad (3.9)$$

where \bar{N}_1 follows from (3.4) and Z' denotes the normalization. If we make use of Stirling's formula

* Note that eqs. (3.2) and (3.25) as well as the equations in section 2 involve the averages in the thermodynamic limit of the stochastic quantities that appear in the master and Fokker-Planck equations.

$$M! \approx \left(\frac{M}{e}\right)^M \quad (3.10)$$

for $N_1!$ and $(N - N_1)!$, the probability (3.9) takes the form

$$p_{st}(N_1) = \frac{1}{Z} \left(\frac{\bar{N}_1}{N_1}\right)^{N_1} \left(\frac{N - \bar{N}_1}{N - N_1}\right)^{N - N_1} \quad (3.11)$$

This may be written

$$p_{st}(N_1) = \frac{1}{Z} \exp\left\{-\frac{1}{k_B T} A(N_1)\right\}, \quad (3.12)$$

where the free energy reads

$$A(N_1) = A(c_1 V) = k_B T V \left\{ \varphi + c_1 \ln \frac{c_1}{\bar{c}_1} + (c - c_1) \ln \frac{c - c_1}{c - \bar{c}_1} + \mathcal{O}\left(\frac{1}{N}\right) \right\}. \quad (3.13)$$

The coefficient φ depends on T and $c = N/V$ only. Eq. (3.12) defines the free energy as $-k_B T$ times the logarithm of the stationary probability of the master equation. Note that this expression coincides with the free energy (2.1) introduced previously on the deterministic level of description apart from terms of $1/N$.

The master equation (3.5) can be expanded into the Kramers-Moyal form¹⁰⁾

$$\dot{p}_i(N_1) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial N_1^n} M_n(N_1) p_i(N_1), \quad (3.14)$$

with the Kramers-Moyal moments

$$\begin{aligned} M_n(N_1) &= V m_n(c_1) = \sum_{N'_1} (N'_1 - N_1)^n W(N_1 \rightarrow N'_1) \\ &= V \{k(c - c_1) + (-1)^n k' c_1\}. \end{aligned} \quad (3.15)$$

For this reaction, the deterministic drift (3.2) equals the first Kramers-Moyal moment

$$m_1(c_1) = k c_2 - k' c_1 = -k' \{c_1 - K(c - c_1)\}. \quad (3.16)$$

In terms of the affinity

$$\chi(c_1) = -\frac{\partial a(c_1)}{\partial c_1} = k_B T \ln \frac{k(c - c_1)}{k' c_1}, \quad (3.17)$$

the deterministic drift may be written

$$m_1(c_1) = \frac{1}{2k_B T} \hat{m}(c_1) \chi(c_1), \quad (3.18)$$

$$\hat{m}(c_1) = 2k' \frac{c_1 - K(c - c_1)}{\ln c_1 - \ln K(c - c_1)} \quad (3.19)$$

The quantity $\hat{m}(c_1)$ is closely connected with the master equation (3.5). Because the transition probability (3.7), (3.8) satisfies the symmetry of detailed balance

$$W(N_1 \rightarrow N'_1) p_{st}(N_1) = W(N'_1 \rightarrow N_1) p_{st}(N'_1), \quad (3.20)$$

the first Kramers-Moyal moment $m_1(c_1)$ may be expressed through higher order moments¹¹⁾

$$m_1(c_1) = \frac{1}{2\pi_{st}(c_1)} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n! V^n} \frac{\partial^n}{\partial c_1^n} m_{n+1}(c_1) \pi_{st}(c_1), \quad (3.21)$$

where

$$\pi_{st}(c_1) = V p_{st}(c_1, V) \propto \exp\left\{-\frac{V}{k_B T} \left[a(c_1) + \mathcal{O}\left(\frac{1}{V}\right) \right]\right\} \quad (3.22)$$

is the stationary probability for the concentration c_1 . If we expand the RHS of (3.21) in terms of $1/V$ we obtain (3.18) with

$$\hat{m}(c_1) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} m_{n+2}(c_1) \left[\frac{\chi(c_1)}{k_B T} \right]^n. \quad (3.23)$$

Using (3.15), $\hat{m}(c_1)$ can be determined explicitly to yield the previous result (3.19). It is now easily checked that the transport coefficient $l(c_1)$ defined by (2.24) and (2.33) is related to $\hat{m}(c_1)$ by

$$l(c_1) = \frac{1}{2k_B T} \hat{m}(c_1). \quad (3.24)$$

This defines the transport coefficient in terms of quantities of the stochastic theory.

3.2. Reversible bimolecular reaction

As a second example we consider the reaction



with $\nu_1 = 1, \nu_2 = -2$. The deterministic flow is given by

$$\dot{c}_1 = -\frac{1}{2}\dot{c}_2 = kc_2^2 - k'c_1, \quad (3.26)$$

and the linear dependence (2.6) between the particle number reads

$$N_2 + 2N_1 = N_2^0 + 2N_1^0 \equiv N \equiv Vc. \quad (3.27)$$

Identifying the particle number N with the progress variable λ , the free energy (2.1) is found to be

$$\frac{A(N_1)}{k_B T} = \phi_0 + N_1 \ln \frac{N_1}{\bar{N}_1} + (N - 2N_1) \ln \frac{N - 2N_1}{N - 2\bar{N}_1} + N_1, \quad (3.28)$$

where the equilibrium value \bar{N}_1 satisfies

$$\frac{\bar{N}_1}{(N - 2\bar{N}_1)^2} = \frac{k}{k'V} = K = \frac{\bar{K}}{V}. \quad (3.29)$$

The ideal dissociation-association reaction (3.25) is modeled by the master equation^{6b)}

$$\begin{aligned} \dot{p}_i(N_1) = & \frac{k}{V} (N - 2N_1 + 2)(N - 2N_1 + 1)p_i(N_1 - 1) \\ & + k'(N_1 + 1)p_i(N_1 + 1) - \frac{k}{V} (N - 2N_1)(N - 2N_1 - 1)p_i(N_1) \\ & - k'N_1 p_i(N_1). \end{aligned} \quad (3.30)$$

The stationary probability of this equation is

$$p_{st}(N_1) = \frac{1}{Z'} \frac{(\bar{N}_1)^{N_1} (N - 2\bar{N}_1)^{N - 2N_1}}{N_1! (N - 2N_1)!}. \quad (3.31)$$

Using Stirling's formula and proceeding as before we find

$$-\frac{k_B T}{V} \ln \pi_{st}(c_1) = a(c_1) + \mathcal{O}\left(\frac{1}{V}\right), \quad (3.32)$$

where $a(c_1)$ equals the free energy density given by (3.28).

The Kramers-Moyal moments are found to be

$$M_n(N_1) = Vm_n(c_1) = V \left\{ k(c - 2c_1) \left(c - 2c_1 - \frac{1}{V} \right) + (-1)^n k' c_1 \right\}, \quad (3.33)$$

and their asymptotic values for large V are

$$m_n^\infty(c_1) = \lim_{V \rightarrow \infty} m_n(c_1) = k(c - 2c_1)^2 + (-1)^n k' c_1. \quad (3.34)$$

An evaluation of (3.21) in the limit $V \rightarrow \infty$ gives

$$m_1^\infty(c_1) = \frac{1}{2k_B T} \hat{m}(c_1) \chi(c_1), \quad (3.35)$$

where

$$\chi(c_1) = -\frac{\partial a(c_1)}{\partial c_1}, \quad (3.36)$$

while

$$\hat{m}(c_1) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} m_{n+2}^{\infty}(c_1) \left[\frac{\chi(c_1)}{k_B T} \right]^n. \quad (3.37)$$

We find

$$\hat{m}(c_1) = 2k' \frac{c_1 - \bar{K}(c - 2c_1)^2}{\ln c_1 - \ln \bar{K}(c - 2c_1)^2}, \quad (3.38)$$

which is again related to the transport coefficient $l(c_1)$ by (3.24).

The above considerations can easily be generalized to multi-component systems undergoing several chemical reactions. The conclusions can be summarized as follows. On the deterministic level the chemical dynamics can be described by the transport laws (2.34). The quantities to be found in these equations have a well-defined meaning within a more detailed stochastic theory described by a master equation. In terms of the stationary probability $\pi_{st}(c_i, V) = V p_{st}(c_i, V)$ of the master equation the free energy density $a(c_i)$ is given by

$$a(c_i) = -\lim_{V \rightarrow \infty} \frac{k_B T}{V} \ln \pi_{st}(c_i, V). \quad (3.39)$$

The free energy defines the thermodynamic forces

$$\chi_i(c_i) = -\frac{\partial a(c_i)}{\partial c_i} \equiv k_B T \tilde{\chi}_i(c_i). \quad (3.40)$$

Further, in terms of the asymptotic values

$$m_{i_1 \dots i_n}^{\infty}(c_k) = \lim_{V \rightarrow \infty} m_{i_1 \dots i_n}(c_k, V) = \lim_{V \rightarrow \infty} \frac{M_{i_1 \dots i_n}(N_k)}{V} \quad (3.41)$$

of the Kramers-Moyal moments of the master equation, the transport coefficients $l^{ij}(c_k)$ are given by ref. 11

$$\begin{aligned} l^{ij}(c_k) &= \frac{1}{2k_B T} \hat{m}_{ij}(c_k) \\ &= \frac{1}{2k_B T} \left\{ m_{ij}^{\infty}(c_k) + \sum_{n=1}^{\infty} \frac{(-1)^n}{(n+1)!} \sum_{i_1 \dots i_n} m_{ij i_1 \dots i_n}^{\infty}(c_k) \tilde{\chi}_{i_1}(c_k) \dots \tilde{\chi}_{i_n}(c_k) \right\}. \end{aligned} \quad (3.42)$$

On a purely deterministic level one might argue that the transport coefficients l^{ij} are not uniquely defined since for multi-component systems

undergoing several reactions there may be different matrices l^{ij} which yield the same fluxes \dot{c}_i upon contraction with χ_j . Such an ambiguity does not arise if we consider (3.42) as the basic definition of the transport coefficients. From the present definitions of χ_j and l^{ij} it is also easily seen that in the limit $V \rightarrow \infty$ the stochastic theory described by the master equation reduces to a deterministic theory described by the transport laws (2.34).

4. Fokker-Planck approximation

The concept of a Fokker-Planck description enjoys great popularity among physicists since explicit calculations are often much easier with the Fokker-Planck equation than with the master equation. Various authors have discussed the Fokker-Planck approximation and its limitations¹¹⁻¹⁵), and we shall not review here this important body of work. Rather, we start out from the observation that Fokker-Planck equations are helpful tools in order to obtain concrete results, in particular for nonlinear systems.

The most commonly used Fokker-Planck equation for chemical reactions is obtained by truncating the Kramers-Moyal expansion of the master equation after the second term.¹⁰), thus disregarding the third and higher order Kramers-Moyal moments. For the bimolecular reaction (3.24) which we shall always consider for illustrative purposes henceforth, one then obtains

$$\dot{\pi}_i(c_1) = \left\{ -\frac{\partial}{\partial c_1} m_1(c_1) + \frac{1}{2V} \frac{\partial^2}{\partial c_1^2} m_2(c_1) \right\} \pi_i(c_1), \quad (4.1)$$

where the drift reads

$$m_1(c_1) = k(c - 2c_1) \left(c - 2c_1 - \frac{1}{V} \right) - k'c_1, \quad (4.2)$$

while the diffusion coefficients is given by

$$m_2(c_1) = k(c - 2c_1) \left(c - 2c_1 - \frac{1}{V} \right) + k'c_1. \quad (4.3)$$

We shall not discuss the results obtained from the Fokker-Planck equation (4.1) in detail, we rather point to the following short-comings.

i) The master equation (3.30) possesses natural boundaries at $N_1 = 0$ and $N_1 = \frac{1}{2}N$ reflecting the finite state space of the closed system. None of these natural boundaries are conserved in the Fokker-Planck approximation (4.1), i.e., the noise drives the system beyond these boundaries.

ii) The stationary probability $\pi_{st}^{FP}(c_1)$ of the Fokker-Planck equation (4.1) does not coincide with the continuum limit (3.32) of the stationary probability of the master equation. This means that a free energy density $a^{FP}(c_1)$ defined

by

$$a^{\text{FP}}(c_1) = -\lim_{V \rightarrow \infty} \frac{k_B T}{V} \ln \pi_{\text{st}}^{\text{FP}}(c_1) \quad (4.4)$$

differs from the correct free energy density $a(c_1)$, and this difference does not vanish in the limit $V \rightarrow \infty$.

While these short-comings of (4.1) are not important near the equilibrium state \bar{c}_1 , the wings of the probability are changed quite dramatically by the Fokker-Planck approximation. This means that, e.g., the calculation of a mean first passage time, where the wings of the probability contribute significantly¹³⁾, cannot reliably be based on a Fokker-Planck equation obtained by truncating the Kramers-Moyal expansion.

In this section we therefore propose a different ad hoc Fokker-Planck approximation to the master equation which essentially overcomes the above short-comings. We follow a general scheme put forward recently³⁾. In that work the connection between a deterministic description in terms of Onsager type transport equations and a stochastic description in terms of a Fokker-Planck process has been investigated on the basis of statistical mechanical considerations. It should be noted that this theory does not necessarily apply to chemical reactions, since the microscopic description is not in terms of continuous phase functions but rather in terms of particle numbers varying in a discrete state space. On the other hand, for large particle numbers the discreteness should be of minor importance. Since the discreteness is also neglected on the deterministic level described by rate laws, a continuous Fokker-Planck description seems to be the natural way to account for fluctuations in a first step towards a more detailed theory.

Following ref. 3, we associate the transport laws (2.34) with a Fokker-Planck equation of the form*

$$\dot{\pi}_i(c_k) = \sum_j \frac{\partial}{\partial c_i} l^j(c_k) \left[\frac{\partial a(c_k)}{\partial c_j} + \frac{k_B T}{V} \frac{\partial}{\partial c_j} \right] \pi_i(c_k). \quad (4.5)$$

For the bimolecular reaction (3.24) the resulting Fokker-Planck equation reads

$$\dot{\pi}_1(c_1) = \left\{ -\frac{\partial}{\partial c_1} b_1(c_1) + \frac{1}{2V} \frac{\partial^2}{\partial c_1^2} b_2(c_1) \right\} \pi_1(c_1), \quad (4.6)$$

with the drift

$$b_1(c_1) = k(c - 2c_1)^2 - k'c_1 + \frac{1}{2V} \frac{\partial \hat{m}(c_1)}{\partial c_1} \quad (4.7)$$

*Note that the form of this Fokker-Planck equation is fixed by the form of the deterministic transport laws (2.34).

and the diffusion

$$b_2(c_1) = 2k_B T l(c_1) = \hat{m}(c_1), \quad (4.8)$$

where $\hat{m}(c_1)$ is given in (3.38).

Clearly, the new Fokker-Planck equation differs from the one obtained by truncating the Kramers-Moyal expansion, and it has the following properties:

i) It is easily seen that (4.5) possesses the stationary probability

$$\pi_{st}(c_i) \propto \exp\left\{-\frac{V}{k_B T} a(c_i)\right\}, \quad (4.9)$$

which coincides with the continuum limit of the stationary probability of the master equation.

ii) The new Fokker-Planck approximation preserves the natural boundaries of the master equation. For the bimolecular reaction (3.25), the stationary probability (4.9) is only defined on the finite state space $0 \leq c_1 \leq \frac{1}{2}c$. Moreover, the diffusion coefficient (4.8) vanishes at the natural boundaries $c_1 = 0$ and $c_1 = \frac{1}{2}c$. In other words, the thermal multiplicative noise characterized by the nonlinear diffusion (4.8) does not drive the system beyond the natural boundaries¹⁶).

iii) In the limit $V \rightarrow \infty$ the Fokker-Planck description reduces to a deterministic description with the correct rate laws.*

On comparing the two Fokker-Planck equations (4.1) and (4.6) we see that the drift terms differ by terms of order $1/V$,

$$b_1(c_1) = m_1(c_1) + \mathcal{O}\left(\frac{1}{V}\right), \quad (4.10)$$

and the diffusion coefficients are related by

$$b_2(c_1) = m_2^\infty(c_1) + \sum_{n=1}^{\infty} \frac{(-1)^n}{(n+1)!} m_{2+n}^\infty(c_1) \left[\frac{\chi(c_1)}{k_B T}\right]^n. \quad (4.11)$$

As usual, we have disregarded the term of order $1/V$ in (4.3) and replaced $m_2(c_1)$ by $m_2^\infty(c_1)$ in eq. (4.1). Then (4.11) follows by virtue of (3.37). Note that the difference between the diffusion coefficients is not of order $1/V$. On the other hand, it is proportional to the deviation from equilibrium as measured by the thermodynamic force $\chi(c_1)$. At $c_1 = \bar{c}_1$ the diffusion coefficients have the same values and the same slopes. [cf. eqs. (2.28), (2.29)].

For the Fokker-Planck equation (4.1) the drift $m_1(c_1)$ coincides by con-

*The newly proposed Fokker-Planck equation (4.6) is essentially determined by the properties i) and iii). A different choice of the diffusion coefficient would either change the deterministic transport law or the leading term of the correct free energy.

struction with the first Kramers–Moyal moment. Therefore, given at time t the single event probability $\pi_t(c_1)$, the rate of the first moment

$$\langle \dot{c}_1 \rangle_t = \langle m_1(c_1) \rangle_t \tag{4.12}$$

is reproduced exactly. This is clearly not the case for the Fokker–Planck equation (4.6) where

$$\langle \dot{c}_1 \rangle_t = \langle b_1(c_1) \rangle_t = \langle m_1(c_1) \rangle_t + \mathcal{O}\left(\frac{1}{V}\right). \tag{4.13}$$

It must be noted, however, that given the single event probability $\pi_{t_0}(c_1)$ at an initial time t_0 , the probability $\pi_t(c_1)$ at later times $t > t_0$ as calculated from the Fokker–Planck equation does not coincide with the master equation evolution of $\pi_t(c_1)$. Hence, there are for times $t > t_0$ corrections of order $1/V$ to the single event probability as calculated from the Fokker–Planck equation which lead to corrections of the same order to the calculated rate of the mean concentration. The difference in (4.13) is therefore not a serious flaw against the newly postulated Fokker–Planck equation (4.6).

Both Fokker–Planck equations (4.1) and (4.6) are ad hoc approximations to the same master equation in the first place, and they can certainly not reproduce all features of the master equation process. They have, however, their limited applicability because:

- i) They possess the same deterministic flow as the full master equation.
- ii) They present a global asymptotic representation¹⁴⁾ of the master equation process in the sense that a L_1 -estimate of the difference $\pi_t^{\text{master}} - \pi_t^{\text{FP}}$ of the corresponding probabilities is small for large V . (Clearly, the ratio $\pi_t^{\text{master}} / \pi_t^{\text{FP}}$ is generally not small.)
- iii) They present a local asymptotic representation of the stationary equilibrium process $c_{\text{st}}(t)$ in the sense of van Kampen¹²⁾, since

$$\lim_{V \rightarrow \infty} V^{1/2}(c_{\text{st}}^{\text{master}}(t) - \bar{c}) = \lim_{V \rightarrow \infty} V^{1/2}(c_{\text{st}}^{\text{FP}}(t) - \bar{c}) = y(t), \tag{4.14}$$

where \bar{c} is the deterministic equilibrium state, while $y(t)$ is a stationary Gauss–Markov process governed by the Fokker–Planck equation

$$\dot{\pi}_t(y) = \left\{ -\frac{\partial}{\partial y} \gamma y + \frac{1}{2} \frac{\partial^2}{\partial y^2} D \right\} \pi_t(y), \tag{4.15}$$

where

$$\gamma = \left. \frac{\partial m_1^\infty}{\partial c_1} \right|_{c_1=c_1}, \quad D = m_2^\infty |_{c_1=c_1}. \tag{4.16}$$

Apart from these common features of both Fokker–Planck equations, the

newly proposed Fokker–Planck equation incorporates the correct form of the free energy and the boundaries of the system. It is thus to be used advantageously in order to determine quantities that sensitively depend on the equilibrium statistics.

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