

# Fluctuations in Diffusion Reaction Systems. I: Adiabatic Elimination of Transport Modes from a Mesoscopic $N$ -Body System and the $\Omega$ -Expansion

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We develop a concise method to compute the corrections to the master equation for chemically reacting systems in particle number space that arise if the system is not a well-stirred tank reactor, but the transport occurs by diffusion. Starting from the master equation in the  $R^N$  space of all reactant particle positions, we expand in inverse powers of the diffusion constant and eliminate all transport modes adiabatically. It is found that the overall effect of spatially nonuniform fluctuations cannot be treated as a mere renormalization of the reaction rate constants. From second order on there appear correction terms with a new structure that corresponds formally to additional virtual reaction paths. An intuitive interpretation along this line is impeded, however, by the formal occurrence of negative reaction rate constants in these terms, i.e., the reaction rate may depend on the concentrations of the final products of the virtual reaction rather than on the ingoing products. We also identify Avogadro's constant as the suitable  $\Omega$  parameter and extend van Kampen's  $\Omega$ -expansion systematically, to spatially continuous systems. This secondary expansion then serves to interpret the corrections to the rate equation, and the average and autocorrelation of the density in the stationary state. It is seen that the limits  $D \rightarrow \infty$  and  $\Omega \rightarrow \infty$  do not commute. The relevant length and time scales are discussed.

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**KEY WORDS:** Diffusion reaction systems; fluctuations; adiabatic elimination; coarse graining; virtual chemical reactions;  $\Omega$ -expansion; hydrodynamic limit.

## 1. INTRODUCTION

Diffusion reaction systems are a particularly well-suited paradigm for the study of fluctuations outside thermal equilibrium. There are no fluctuation-

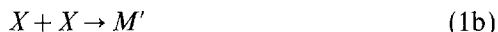
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dissipation theorems available then and all information about the fluctuations must be derived from a somewhat microscopic description of the system. The advantage of diffusion reaction systems is that they allow a rather tractable mesoscopic description that is inherently irreversible and stochastic like the Boltzmann equation and still retains all correlations of the reactant particle positions similar to the Liouville equation.

We consider reactant molecules ("reactants") that are suspended in a fluid medium at rest in which they perform Brownian motion. Our time scale of interest is much slower than the decay of all fluid–fluid and reactant–fluid correlations. On our time scale the medium serves only as an ether in which the reactants diffuse. The repeated randomness assumption is made only for collisions with medium particles, so the model equations are irreversible and stochastic. On the contrary, we do not impose the repeated randomness for reactant–reactant collisions, but treat the reactants on the  $N$ -body level. This mesoscopic description (between microscopic and macroscopic) allows the study of diffusion-controlled reactions and of the limitations of the "local equilibrium" concept, which does not apply in the presence of such reactions.

In this paper, we solve the fundamental problem of coarse graining by the systematic adiabatic elimination<sup>(1)</sup> of transport modes and take account of all spatially nonuniform fluctuations. We consider the reaction scheme



Both reactions are considered irreversible and the concentration of  $M$  is assumed to remain constant without fluctuations, while  $M'$  is continuously drained from the system. The only variable quantity of interest is the density  $\rho$  of  $X$ .

If the system is well stirred so that it is kept uniform for all times,  $\rho$  is the same throughout the system and obeys macroscopically the reaction rate law<sup>2</sup>

$$\partial_t \rho = b - a\rho^2 \quad (2)$$

The fluctuations are then also uniform in space and all information about them can be derived together with (2) by van Kampen's  $\Omega$ -expansion<sup>(2)</sup> of the master equation for the uniform system:

$$\partial_t P(N, t) = \frac{bV}{m} (\mathbb{E}^{-1} - 1) P(N, t) + \frac{am}{V} (\mathbb{E}^2 - 1) \binom{N}{2} P(N, t) \quad (3a)$$

<sup>2</sup> By density we mean the mass density, i.e., total mass of  $X$  reactants divided by the volume of the system. The number density can be computed from macroscopic measurable quantities only by the use of Avogadro's constant and is therefore conceptually not a macroscopic quantity.

In this equation<sup>3</sup>  $P(N, t)$  is the probability that at time  $t$  the system contains exactly  $N$  reactants of sort  $X$ . Here  $V$  denotes the volume of the system,  $m$  is the mass of one  $X$  molecule, and the step operator  $\mathbb{E}$  is defined by  $\mathbb{E}f(N) = f(N+1)$  for any function  $f(N)$ . The  $\Omega$  parameter is usually identified with the volume  $V$ , so that the  $\Omega$ -expansion becomes more specifically a system-size expansion. The density  $\rho$  in (2) emerges from this as

$$\rho = \lim_{V \rightarrow \infty} \frac{\langle N \rangle m}{V} \quad (3b)$$

If the system is not well stirred, but the transport in the system occurs by diffusion, Eq. (2) is readily generalized. One defines a local density  $\rho(\mathbf{r}, t)$  which changes locally due to the reaction process according to (2), and simply adds the remaining part of the change in  $\rho(\mathbf{r}, t)$  that is due to diffusion:

$$\partial_t \rho(\mathbf{r}, t) = D \Delta_{\mathbf{r}} \rho(\mathbf{r}, t) - a \rho^2(\mathbf{r}, t) + b \quad (4)$$

Similar to the Navier–Stokes equations, Eq. (4) can be derived from a more microscopic description on the  $N$ -body level if one neglects all correlations between particle positions.<sup>(3)</sup> We will therefore refer to Eq. (4) as the hydrodynamic equation for the diffusion reaction system. This approximation can be made systematically<sup>(4)</sup> and is valid if the bimolecular reaction step is not in the least diffusion-controlled, i.e., if every  $X$  particle meets many others by diffusion before it reacts eventually. However, unlike the well-stirred case, in this derivation the density  $\rho$  does not emerge as a limit of the average of a fluctuating quantity, but as the probability density to find  $X$  at position  $\mathbf{r}$  and time  $t$ . Therefore, the treatment of the fluctuations is not a simple generalization of the expansion in inverse powers of the system size  $V$  that one makes for (2).

In order to improve on both, (3) and (4) without descending to the  $N$ -body level, one would like to include selectively the relatively small and slow long-range fluctuations in the description and avoid the relatively large and fast short-range fluctuations that occur on the length scale of the distance between nearest neighbor reactants, i.e. one would like to use a coarse-grained description. How such a reduced description can be derived from the description on the  $N$ -body level is the subject of this paper. For

<sup>3</sup> We use here the more appealing product  $N(N-1)/2$  in the bimolecular reaction term, although there is no experimental evidence against using  $N^2/2$ . The difference does not show in the leading order of the fluctuations and the next order effects have not yet been observed in real chemical systems.

simplicity, we take the length scale of our coarse graining to be equal to the size of the system, so that the reduction of the description amounts to the systematic adiabatic elimination<sup>(1)</sup> of all transport modes. All spatially non-uniform fluctuations are accounted for, although they do not appear explicitly in the reduced description.

The common description of the spatially nonuniform fluctuations starts from a coarse grained description that is obtained in an unsystematic way: the system volume is divided into cubic cells of size  $l^d$  ( $d$  is the dimensionality), and the master equation (3) is postulated for the change in the number of particles in each cell.<sup>(5-8)</sup> Diffusion effects are taken into account by a probability rate for jumps of particles from each cell to the adjacent cells. In the following, we explain briefly why this approach is not satisfactory and how the problems are to be resolved.

The cellular description for our particular system with the reactions (1a)–(1b) is the multivariate master equation

$$\begin{aligned} \partial_t P(\{N_{\mathbf{r}}\}, t) = & D l^{-2} \sum_{\mathbf{r}} \sum_{\Delta \mathbf{r}} (\mathbb{E}_{\mathbf{r}+\Delta \mathbf{r}}^{-1} \mathbb{E}_{\mathbf{r}} - 1) N_{\mathbf{r}} P(\{N_{\mathbf{r}}\}, t) \\ & + a m l^{-d} \sum_{\mathbf{r}} (\mathbb{E}_{\mathbf{r}}^2 - 1) \binom{N_{\mathbf{r}}}{2} P(\{N_{\mathbf{r}}\}, t) \\ & + \frac{b l^d}{m} \sum_{\mathbf{r}} (\mathbb{E}_{\mathbf{r}}^{-1} - 1) P(\{N_{\mathbf{r}}\}, t) \end{aligned} \quad (5)$$

$N_{\mathbf{r}}$  is the number of X reactants inside a  $d$ -dimensional cubic cell with volume  $l^d$  that is centered at  $\mathbf{r}$ . The summation index  $\Delta \mathbf{r}$  points in turn from one cell center to each of the  $2d$  nearest neighbor cell centers, so  $|\Delta \mathbf{r}| = l$ . The  $\mathbb{E}_{\mathbf{r}}$  denotes the step operator with respect to  $N_{\mathbf{r}}$ , so that for any function  $f$

$$\mathbb{E}_{\mathbf{r}} f(\dots, N_{\mathbf{r}}, \dots) = f(\dots, N_{\mathbf{r}} + 1, \dots) \quad (6)$$

Furthermore, periodic boundary conditions are assumed, so that the system as a whole is a  $d$ -dimensional torus. The jump rates depend the lattice constant  $l$ , so that: (a) when viewed on a length scale much larger than  $l$ , the random walk of the reactants between the cells, which is described by the first line of the right-hand side of Eq. (5), appears as a diffusion process with diffusion constant  $D$ , and (b) if the cells are so large that they contain many reactants ( $N_{\mathbf{r}} \gg 1$ ), the constants  $a$  and  $b$  are the reaction rate constants that appear in the phenomenological macroscopic reaction rate law (2) for each cell.

Technically, the solution of (5) appears to be just more difficult than solving (3a) (in general, any master equation that describes bimolecular

reactions cannot be solved in closed form<sup>(2)</sup>). Physically, however, (5) is problematic, because the coefficients  $a$  and  $b$  are usually only approximately defined, namely up to their leading order in  $\Omega^{-1/2}$ , which appears in the rate equation (2). For the master equation in number space (3a), the only consequence of the indefinite higher orders of  $a$  and  $b$  is that only the lower orders of van Kampen's  $\Omega$ -expansion are physically relevant. The dilemma of all cellular models like (5) is that the above mentioned requirement (a) for the jump rates in (5) fixes  $D$  only asymptotically for small  $l$ , i.e., up to relative order  $(lm^{1/d}\rho_s^{-1/d})^{1/2}$ , while (b) fixes  $a$  and  $b$  only asymptotically for large  $l$ , i.e., up to relative order  $(lm^{1/d}\rho_s^{-1/d})^{-d/2}$ , where  $m^{1/d}\rho_s^{-1/d}$  is a mesoscopic characteristic length in the problem, e.g.,  $\rho_s/m$  is the average number density of reactants in the stationary state of a well-stirred system.

The common remark<sup>(5)</sup> is that one should use an intermediate value for  $l$  which is large enough so that each cell contains many particles and still small enough so that diffusion is truly modeled on a macroscopic scale. This amounts to a coarse graining of the actual microscopic distribution of  $X$  mass so that all reactants in a same cell overlap. However, in common chemical reactions, a reactant does not have many possible reaction partners available at the same time with which it has equal probability to react. Mostly, paired reactants undergoing a reactive collision are each other's nearest neighbor at that moment. So there is no overlap range of intermediate values for  $l$  where one can use (5) and also truly describe diffusion of the individual reactants on the relevant length scale, which is given by the average distance between nearest neighbor reactants.

An excuse for the spatially discrete description is<sup>(6)</sup> that there is a minimal length scale below which the one-particle diffusion equation is not valid. The diffusion equation approximates the actual Brownian motion of the reactants no better than a random walk with steps of that length. This length is the velocity persistence length<sup>(9)</sup> of the Brownian particle and it is determined by the reactant–fluid interaction and not related to the next nearest neighbor distance among reactants. The correct description on this more microscopic length scale is the many-particle Kramers equation,<sup>(10)</sup> which is much more complicated than (5). We assume here that the velocity persistence length for the reactants is much smaller than the typical nearest neighbor distance between them. The many-particle Kramers equation then reduces to the many-particle diffusion equation, and corrections due to the physically imperfect approximation of the one-reactant motion can be absorbed into the parameters that describe the reactant–reactant pair interaction.<sup>(11)</sup>

We use the simple one-particle diffusion equation as a model for the Brownian motion transport and take it seriously on all length scales. This

means that we take the limit  $l \rightarrow 0$  in the diffusion term of (5). The remaining problem is to describe on a mesoscopic scale the reaction interaction between pairs of reactants.

The  $l \rightarrow 0$  limit of the reaction terms in (2) cannot be used for a mesoscopic description of the reaction interaction. This is most evident for  $d > 1$ , because then in the limit  $l \rightarrow 0$  the bimolecular reaction term predicts no reaction at all. In this limit, the reactants are point particles and as such have zero probability to meet by diffusion. The true reaction term then contains contributions proportional to  $1/(l-l_0)$ , where  $l_0$  is a microscopic length like the diameter of the reactant particles. This contribution is not detectable for macroscopic cells, but diverges well before  $l \rightarrow 0$ .

In order to be definite on a mesoscopic length scale, we present in Section 2 a plausible picture of the reaction mechanism and thereby fix the form of the reaction term. Also, we specialize to a one-dimensional system in order to keep the notation simple. The adiabatic elimination scheme for our case is explained in Section 3. In Section 4 we present the explicit form of the correction terms up to order  $1/D^2$  that arise because the partial equilibrium with respect to diffusion is only incompletely attained between successive reaction events and the repeated randomness assumption for the particle positions inherent in (3) holds only approximately. The corrections can be interpreted most easily by the  $\Omega$ -expansion, and in Section 5 we show how to include them into this secondary expansion. In Section 6 we discuss the correction of order  $1/D$  and remark on the applicability of other fluctuation treatments to diffusion reaction systems. In Section 7 we explain the additional features that appear in the corrections of order  $1/D^2$  and higher. We isolate the dominant macroscopic effects of these corrections and show the limitations of the  $\Omega$ -expansion of these corrections. We remark in Section 8 on the changes that appear if our treatment is applied to higher dimensions. Finally, we summarize our findings in Section 9 and compare our treatment to other expansions that are used in the kinetic theory of fluids.

## 2. A PLAUSIBLE MICROSCOPIC DESCRIPTION IN A CONVENIENT FORM

Our formalism does not depend on the dimensionality; therefore, we consider explicitly only the one-dimensional version of the problem and defer our remarks on higher dimensions to Section 8.

A number  $N$  of point reactants  $X$  diffuse on a ring of length  $2L$ . Any pair of reactants at a distance  $r$  apart has a probability rate  $A(r)$  to react. After a reaction event has taken place, the reaction product is no longer accounted for. Also, for every infinitesimal ring element  $dr$  there is the

probability rate  $B dr$  for the spontaneous creation of a new reactant. The master equation for this system reads

$$\begin{aligned} \partial_t P_N(R_1, \dots, R_N; t) = & D \sum_i A_{R_i} P_N - \sum_{1 \leq i < j \leq N} A(R_i - R_j) P_N \\ & + \frac{1}{2} \int dR_{N+1} \int dR_{N+2} A(R_{N+1} - R_{N+2}) P_{N+2} - P_N \int dR_{N+1} B \\ & + B \sum_{1 \leq i \leq N} P_{N-1}(R_1, \dots, \hat{R}_i, \dots, R_N; t) \end{aligned} \quad (7)$$

where the normalization of the functions  $P$  is given by

$$\sum_{N=0}^{\infty} \frac{1}{N!} \int dR_1 \cdots \int dR_N P_N(R_1, \dots, R_N; t) = 1 \quad (8)$$

All integrations are extended over the whole system. This equation can be obtained as the  $l \rightarrow 0$  limit of (5) if one allows for a reaction probability rate  $A(R - R')$  for any pair of particles that reside in the cells centered at  $R$  and  $R'$ , respectively. Also, the independent variables have been changed from the occupation numbers  $N_r$  to the positions  $R_1, \dots, R_N$  of those cells that are occupied. The particles bear no labels in this description, so  $P_N(R_1, \dots, R_N; t)$  is always symmetric in all its position variables, and the inverse factorial in (6) corrects for the multiple counting. Apart from diffusion, the probability that there are exactly  $N$  particles in the system at positions  $R_1, \dots, R_N$  changes through reactions:

1. There is a decrease because the particles at any two of these positions can react and also because an additional particle can be created at any additional position  $R_{N+1}$ .
2. There is an increase because there may have been two more particles at positions  $R_{N+1}$  and  $R_{N+2}$  that have just reacted. Also there may have been particles at all  $N$  but one positions, namely at  $R_1, \dots, \hat{R}_i, \dots, R_N$ , and there has been a particle created at  $R_i$ .

It is convenient to introduce the generating functional  $G$  for the functions  $P_N$ :

$$G(\{x(r)\}, t) = P_0 + \sum_{N=1}^{\infty} \frac{1}{N!} \int dR_1 \cdots \int dR_N x(R_1) \cdots x(R_N) P_N(R_1, \dots, R_N; t) \quad (9a)$$

$$G(\{x(r)\}, t)|_{x(r)=1} = 1 \quad (9b)$$

and

$$P_N(R_1, \dots, R_N; t) = \delta_{x(R_1)} \cdots \delta_{x(R_N)} G(\{x(r)\}; t)|_{x(r) \equiv 0} \quad (9c)$$

where  $\delta$  stands for functional derivations.

For systems in the thermodynamic limit ( $L \rightarrow \infty$ ,  $\langle N \rangle \rightarrow \infty$ ,  $\langle N \rangle/L = \text{const.}$ ) it is more common to use the functional derivatives:

$$f_N(R_1, \dots, R_N; t) = \delta_{x(R_1)} \cdots \delta_{x(R_N)} G(\{x(r)\}; t)|_{x(r) \equiv 1} \quad (9d)$$

The functions  $f_N$  are multiple point densities, i.e.,  $f_2(R_1, R_2, t)$  is the probability density to find two reactants at positions  $R_1$  and  $R_2$  at time  $t$ , regardless of all other reactants in the system. We will not use these derivatives explicitly in the following nor will we take the thermodynamic limit, but for our discussions it is helpful to notice that the functions  $f_N$  factor like  $f_N = (f_1)^N$  if the reactant positions are uncorrelated and if the probability distribution for their number is of the Poisson type. So all information about correlations between reactant positions is contained in the space dependence of the function  $f_2$  and higher ones. Notice also, that the functions  $f_N$  are not normalized in any way.

In terms of  $G$ , the master equation (7) reads

$$\begin{aligned} \partial_t G(\{x(r)\}, t) &= D \int dr x(r) A_r \delta_{x(r)} G \\ &+ \frac{1}{2} \int dr \int dr' A(r-r') [1 - x(r)x(r')] \delta_{x(r)} \delta_{x(r')} G \\ &+ B \int dr [x(r) - 1] G \end{aligned} \quad (10)$$

Furthermore, it is convenient to Fourier transform with respect to  $r$ :

$$\hat{x}(k) = \frac{1}{2L} \int dr e^{-ikr} x(r) \quad (11a)$$

$$x(r) = \sum_k \hat{x}(k) e^{ikr} \quad (11b)$$

$$\delta_{x(r)} = \frac{1}{2L} \sum_k e^{-ikr} \partial_{\hat{x}(k)} \quad (11c)$$

$k$  assumes all discrete values, so that  $kL/\pi$  is integer. For real  $x(r)$ ,  $\hat{x}(k) = \hat{x}(-k)$ , but  $\hat{x}(k)$  and  $\hat{x}(-k)$  are treated as independent variables. Equation (10) then takes the form



$$\begin{aligned} \partial_t G(\{\hat{x}(k)\}, t) = & -D \sum_k k^2 \hat{x}(k) \partial_{\hat{x}(k)} G \\ & + \frac{1}{2} \sum_{k_1, k_2, k_3, k_4, k_5} \hat{A}(k_1) [\delta(k_2) \delta(k_3) - \hat{x}(k_2) \hat{x}(k_3)] \\ & \times \delta(k_1 + k_2 - k_4) \delta(k_1 - k_3 + k_5) \partial_{\hat{x}(k_4)} \partial_{\hat{x}(k_5)} G \\ & + 2LB[\hat{x}(0) - 1]G \end{aligned} \tag{12}$$

where  $\delta(k) = 1$  if  $k = 0$ , and 0 if  $k \neq 0$ .

Readers familiar with the expansion in the inverse system size might expect a  $(2L)^{-1}$  dependence in the  $k_1 = 0$  term in the second line of (12). It is hidden, in that for a given choice of  $A(r)$ ,  $\hat{A}(k) \sim (2L)^{-1}$ . The  $L$ -dependence for a sum over a given range of  $k$ -values is different, however, because the spacing of the allowed  $k$ -values depends on  $L$ .

### 3. THE ADIABATIC ELIMINATION SCHEME

The concept of partial equilibrium leads to good approximations if the fast variables in the problem belong to the first category in van Kampen's classification<sup>(1)</sup> (see also Ref. 12), i.e., if the time development operator  $H$ , in the dynamic equation for  $G$

$$\partial_t G = HG \tag{13}$$

can be split into a dominating part  $(1/\varepsilon)T$  with eigenvalues that are either zero or have comparatively large negative real parts (in our case the transport operator) and a complementary part  $R$  with eigenvalues that are comparatively small in modulus (in our case the reaction operator):

$$H = \frac{1}{\varepsilon}T + R \tag{14}$$

Starting from an arbitrary initial condition, the system then first goes through a transient regime during which the fast part of  $G$ , called  $FG$ , decays.  $F$  is the projection operator on the nonzero subspace of  $(1/\varepsilon)T$ .<sup>4</sup> The remaining slow part of  $G$ , called  $SG$ , lies entirely in the subspace of  $(1/\varepsilon)T$  and then develops more slowly in time, being governed mainly by  $R$ . The adiabatic elimination scheme is the systematic extraction of the reduced dynamic equation for  $SG$  for the time after the transient from the full equation (13).

<sup>4</sup> In general,  $F$  projects on the left nonzero subspace,<sup>(1)</sup> but here the projectors on the left and right nonzero subspaces are identical.

The complementary pair of projection operators  $S$  and  $F$  are uniquely defined<sup>5</sup> for any given choice of how to split  $H$ :

$$SG = \lim_{t \rightarrow \infty} e^{Tt}G \quad (15a)$$

$$S + F = 1, \quad S \cdot S = S, \quad F \cdot F = F \quad (15b)$$

Equation (15a) is a defining recipe for the preparation of partial equilibrium: halt all slow processes (small eigenvalues) in the system and let all fast processes proceed until they have come to their long-time limit halt. Of course, the partial equilibrium concept applies only if the fast processes do lead to a stationary long-time limit so that the limit in (15a) exists.

The classification into fast and slow processes may seem as arbitrary as the selection of fast and slow variables in the Mori–Zwanzig scheme. However, it amounts to a certain scaling of the parameters in the operator  $H$  with the dimensionless parameter  $\varepsilon$ , and from this scaling we will read off the regime where the chosen partial equilibrium is a good approximation (see end of Section 7).

Once we have identified the projection operators  $S$  and  $G$ , we are free to choose the basis in the argument space of  $G$ . It is most convenient to choose the independent variables  $x$  so that  $T$  is block-diagonal<sup>(12)</sup>; the variables  $x$  can then be grouped in  $x_s$  and  $x_f$  (according to whether  $\delta_x G$  changes slowly or quickly during the transient), so that

$$SG(x_s, x_f; t) = G(x_s, 0; t) \quad (16)$$

The independent variables in (12) have already been chosen accordingly.

In our case, the fast process is diffusion, so that  $(1/\varepsilon)T$  is the transport operator in the first line of (12):

$$\frac{1}{\varepsilon} TG(\{\hat{x}(k)\}, t) = \partial_z|_{z=0} G(\{\hat{x}(k) \exp(-Dk^2 z)\}, t) \quad (17)$$

There are two possible reasons that lead to large eigenvalues for the operator  $(1/\varepsilon)T$  and they correspond to two different scalings:

1. Either the system is small and one scales  $L = \varepsilon^{1/2}\bar{L}$ ,  $D = \bar{D}$ , where the barred quantities are scale-invariant. The absolutely smallest nonzero eigenvalue of  $(1/\varepsilon)T$  is then  $(1/\varepsilon)\pi^2/\bar{L}^2$ . However, the system size enters in several other ways into the dynamic Eq. (13) and the transport operator  $T$  would not be singled out according to (14), but the reaction operator  $R$  would still depend on  $\varepsilon$ .

<sup>5</sup> Equation (6.4.29) in Ref. 8. In general the limit in (15a) need not exist. See Ref. 1 for details.

2. Or the diffusion constant is large and one scales  $L = \bar{L}$ ,  $D = (1/\varepsilon)\bar{D}$ . This is meant here.

The difference between the two scalings shows that the elimination scheme is not a simple expansion in powers of the system size. We will keep the system size constant and finite throughout.

The explicit form of  $SG$  follows from (17) and (15a):

$$SG(\{\hat{x}(k)\}, t) = G(\{\hat{x}(k) \delta(k)\}, t) \quad (18)$$

The common term “fast variables”<sup>6</sup> denotes those system variables that approach a limit during the transient regime. In our case, they are all partial derivatives (all orders) of  $G$  with respect to  $\hat{x}(k)$ ,  $k \neq 0$ . The derivatives in first order are the fast variables that one would expect from the hydrodynamic Eq. (4), namely the Fourier components of  $\rho$  for  $k \neq 0$ . The higher order derivatives of  $G$  with respect to  $\hat{x}(k)$ ,  $k \neq 0$  describe in particular the correlations between reactant positions (see Eq. (9d)). These correlations decay by diffusion.

The adiabatic elimination proceeds formally as follows: First write out the coupled equations for the slow and fast parts of  $G$ :

$$\partial_t SG = SRSG + SRFG \quad (19a)$$

$$\partial_t FG = \frac{1}{\varepsilon} TFG + FRSG + FRFG \quad (19b)$$

Eq. (19a) describes the dynamical behavior of the system as it appears in the slow subspace, in our case the number space: the first term on the right-hand side  $SRSG$  is the same as the right-hand side of the master equation (3a) in number space for a well-stirred system. The second term comprises all the corrections to this that arise due to correlations between reactant positions. Eq. (19b) describes the dynamical behavior in the fast subspace of correlations between reactant positions: the first term on the right-hand side  $(1/\varepsilon) TFG$  describes the fast decay of the correlations. The second term  $FRSG$  represents the correlations that arise constantly by reaction events—even if the system starts to evolve from a well-stirred initial state  $SG$ . The third term  $FRFG$  describes the modification of correlations between reactant positions that occur due to reactions.

In the limit of infinitely fast diffusion  $\varepsilon = 0$ . Following a reaction event, the system attains instantaneously the partial equilibrium with respect to diffusion. The first term on the right-hand side of (19b) ensures then that

$$\lim_{\varepsilon \rightarrow 0} FG = 0 \quad (20)$$

<sup>6</sup> First category in van Kampen's classification.

for all times. The dynamics of the correlations as described by the other two terms is irrelevant in this limit, because the correlations decay instantaneously and  $FG = 0$ . So the possible reaction partners for any one reactant are then distributed uniformly and the system behaves as if it is well-stirred,<sup>(6,8)</sup> i.e., (19a) is then equivalent to (3a).

If diffusion is not infinitely fast, it takes a time of order  $\varepsilon$  for the part  $FG_0$  of the full general initial condition  $G(\{\hat{x}(k)\}, 0) = G_0(\{\hat{x}(k)\})$  to decay. During this transient,  $FG$  couples to  $SG$  via the last term in (19a). So the long-time dynamics of  $SG$  does not only depend on  $SG_0$  but also from order  $\varepsilon$  on  $FG_0$ . In the following, we only show how to extract the reduced description for the dynamics of  $SG$  after the transient. We do not discuss the effective initial condition  $SG_{eff}$  for  $SG$  to which this reduced description extrapolates back at time  $t = 0$ . In order to obtain  $SG_{eff}$  from  $G_0$ , one would have to solve the full initial value problem for (13).

The computation of higher orders in  $\varepsilon$  relies on the fact that (19b) couples different orders of  $FG$  in  $\varepsilon$ , so (19a) and (19b) together constitute a recursion relation that allows one to determine successively higher orders in  $\varepsilon$  of the reduced dynamic equation for the partial equilibrium distribution  $SG$  in terms of the lower orders. The order linking step in the recursion is

$$FG + O(\varepsilon^{n+1}) = \varepsilon T^{-1}[-FRSG + (\partial_t - FR)FG + O(\varepsilon^n)] \quad (21)$$

where  $T^{-1}$  operates only on functions that lie entirely in the nonzero subspace of  $T$ . The first explicit steps of the scheme are as follows:

In first order in  $\varepsilon$  one deduces from (19b) and (20)

$$FG = -\varepsilon T^{-1}FRSG + O(\varepsilon^2) \quad (22)$$

This is substituted in (19a) and in first order in  $\varepsilon$  the system behaves on the slow time scale according to

$$\partial_t SG = SRSG - \varepsilon SRT^{-1}FRSG + O(\varepsilon^2) \quad (23)$$

To obtain the second-order approximation, one uses (19b), now together with (22) instead of (20), to get

$$FG = -\varepsilon T^{-1}FRSG + \varepsilon^2(T^{-1}FRFT^{-1}FRSG - T^{-2}FRSRSG) + O(\varepsilon^3) \quad (24)$$

This is then substituted into (19a):

$$\begin{aligned} \partial_t SG = & SRG - \varepsilon SRT^{-1}FRSG \\ & + \varepsilon^2 SR(T^{-1}FR)^2 SG - \varepsilon^2 SRT^{-2}FRSRSG + O(\varepsilon^3) \end{aligned} \quad (25)$$

This scheme can be pursued *ad infinitum* and the resulting exact dynamic equation for  $SG$  is of the form

$$\partial_t SG = SR \sum_{n=0}^{\infty} \varepsilon^n K_n SG \tag{26}$$

We do not explicitly use any higher order than second in  $\varepsilon$ . The general recursion relation for the operators  $K_n$  was already derived by Bloch<sup>(13)</sup>:

$$K_n = - \sum_{\nu=2}^{n-1} K_{\nu} + \varepsilon T^{-1} \sum_{\nu=1}^{n-1} \left( -FRK_{\nu} + \sum_{\mu=0}^{\nu-1} K_{\nu-\mu} SRK_{\mu} \right) \tag{27}$$

with  $K_0 = 1$ . Note that through the  $\mu = 0$  term in (27) there enters the general term

$$\varepsilon^n SRT^{-n}FRS(SRS)^{n-1} \tag{27a}$$

into the dynamic Eq. (26) at order  $\varepsilon^n$ . We will come back to this term later in connection with the  $\Omega$  expansion at the end of Section 7 and in the concluding remarks of Section 9.

#### 4. THE EXPLICIT CORRECTION TERMS

The explicit form for the zeroth order in  $\varepsilon$  for (19a) is

$$SRK_0 SG = \frac{1}{2} \hat{A}(0) [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG + 2LB [\hat{x}(0) - 1] SG \tag{28}$$

It is intuitively clear that in this order only the integral of  $A(r)$  is relevant, since in this order no correlations between particle positions are taken into account. Comparison of (28) with (3) shows that

$$\lim_{\varepsilon \rightarrow 0} a \frac{m}{V} = \hat{A}(0) \quad \text{and} \quad \lim_{\varepsilon \rightarrow 0} b \frac{V}{m} = 2LB \tag{29}$$

The major computational difficulty in obtaining higher orders in  $\varepsilon$  is to invert the dominating part  $(1/\varepsilon)T$  of the full operator  $H$ . In our case, this is easy with the help of (17):

$$\varepsilon T^{-1} FG(\{\hat{x}_k\}, t) = \int_0^{\infty} dz [G(\{\hat{x}(k) \exp(-Dk^2z)\}, t) - G(\{\hat{x}(0) \delta(k)\}, t)] \tag{30}$$

This expression shows that the functional  $T^{-1}FG$  differs from  $FG$  in that its dependence on  $\hat{x}(k)$  for high  $k$  is damped. In accordance with this, the

excitations of the fast modes from diffusive equilibrium are least important in the correction terms. These correlations diffuse away most rapidly. More details are given in Ref. 14.

The basic explicit structure of the correction terms of order  $\varepsilon^n$  in (20), namely  $SRK_n SG$ , can be seen in our problem from the terms up to second order:

$$\begin{aligned} SRK_1 SG &= -\varepsilon SRT^{-1}FRSG \\ &= -\sum_{k \neq 0} \frac{1}{Dk^2} \hat{A}^2(k)[1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG \end{aligned} \quad (31)$$

$$\begin{aligned} SRK_2 SG &= \varepsilon^2 SR(T^{-1}FRT^{-1}FR - T^{-2}FRSR) SG \\ &= \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{1}{8D^2 k_1^2 k_2^2} \hat{A}(k_1) \hat{A}(k_1 + k_2) \hat{A}(k_2) [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG \\ &\quad - \sum_{k \neq 0} \frac{1}{8D^2 k^4} \hat{A}^2(k) \frac{1}{2} \hat{A}(0) [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG \\ &\quad - \sum_{k \neq 0} \frac{1}{8D^2 k^4} \hat{A}^2(k) \cdot 2LB[1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 [\hat{x}(0) - 1] SG \end{aligned} \quad (32)$$

where we have assumed for simplicity that  $A(r)$  is symmetric and real, i.e.,  $\hat{A}(k) = \hat{A}(-k)$ .

Before we can study the correction terms (31) and (32) in detail in Sections 6 and 7, we first have to discuss the application of van Kampen's  $\Omega$ -expansion to diffusion-reaction systems.

## 5. THE $\Omega$ -EXPANSION FOR DIFFUSION REACTION SYSTEMS

We start by stating the obvious. The fluctuating deviations from the hydrodynamic equations that govern our macroscopic world are number fluctuations. They are small by everyday measures because Avogadro's number  $N_A$  is large, and if we imagined a different world which is macroscopically identical to ours but with a much larger numerical value of  $N_A$ , the hydrodynamic equations would be the same, only the fluctuations would be scaled down. In the limit  $N_A \rightarrow \infty$  the fluctuations would disappear altogether, because all matter would then be truly continuous and not chunked into molecules. This property of the parameter  $N_A$  meets precisely the requirements<sup>(2)</sup> for the  $\Omega$  parameter. The  $\Omega$ -expansion is the expansion of the master equation around the limit  $\Omega \rightarrow \infty$ . It serves to derive systematically the hydrodynamic equations and all statistical information about the fluctuations.

For reaction systems with no spatial correlations between reactants, e.g., in the limit  $D \rightarrow \infty$  of a diffusion reaction system,  $\Omega$  can also be chosen as the scaling parameter of the volume of the system, so that the  $\Omega$ -expansion becomes more specifically a system-size expansion. This interpretation is usually preferred because the system size is easily varied both in experiment and thought, while  $N_A$  is a constant in nature. However, it is evident from the volume dependence of (29) that the system-size expansion is not possible if the diffusion constant is finite.<sup>7</sup> The terms in (31) diverge in the limit of infinite system-size<sup>(6)</sup>: the two derivative operators with respect to  $\hat{x}(0)$  give two extensive factors, namely, the total number of particles in the system. This is compensated because  $\hat{A}(k) - (2L)^{-1}$  for any reasonable  $A(r)$ , e.g.,  $A(r) = \lambda\theta(\sigma - |r|)$ ,  $-L < r < L$ . Finally, both inverse factors  $k$  contribute one factor  $L$  because during the summation  $k \cdot L/\pi$  assumes all integers (which do not depend on  $L$ ). In comparison to (28), which is of first order in the system-size, (31) is of second order; higher order terms in the expansion (26) are of increasingly higher order in  $L$ , and, without regard to the dimension of the system, the common expansion in inverse powers of the system-size cannot be carried out on the higher order terms in (26)<sup>(6)</sup>. This is because the decay time for the slowest transport mode is large for large systems, while we assumed it to be small in our primary expansion, namely the adiabatic elimination scheme. We therefore turn back to the scaling of Avogadro's number instead of the system size and keep the decay time for the slowest mode constant.

First, we need the correct scaling of the parameters in (10). Both the system size  $2L$  and the diffusion constant  $D$  can be measured macroscopically, e.g.,  $D$  can be measured via the decay time of the slowest transport mode in the limit of low concentration, so that all interactions between reactants can be neglected.  $D$  is a macroscopic parameter that describes the transport of single reactants in the medium. So the parameters  $D$  and  $L$  are scale independent.<sup>(8)</sup>

The parameter  $B = b/m$  measures a number rate density that cannot be measured macroscopically, in contrast to the mass rate density  $b$ . We scale, therefore,

$$m = \bar{m}\Omega^{-1}, \quad B = \Omega b/\bar{m} \quad (33)$$

where  $\bar{m}$  is a macroscopic mass, such as the mass of 1 mole of reactant substance X, and  $\bar{m}$  does not depend on  $\Omega$ . All number fluctuations in the

<sup>7</sup> In higher dimensions the divergence for large system size occurs at higher order corrections of the adiabatic elimination scheme.

<sup>8</sup> The diffusion constant of particles in a fluid with a given viscosity does depend on the size of the particles. In order to keep the macroscopic appearance of our system independent of  $\Omega$  and isolate the effects of number fluctuations in the number of reactants in the system in a real experiment, one would have to adjust the viscosity to the size of the reactants.

amount of X mass that is generated by the process (1a) in a certain time interval disappear in the limit  $\Omega \rightarrow \infty$ .

The scaling of the coefficients  $\hat{A}(k)$  for the bimolecular reaction term is more intricate, because the mesoscopic nature of the reaction remains to be fully specified in its  $\Omega$  dependence. Only the scaling of  $\hat{A}(0)$  is fixed by (29).

In one dimension, a particularly simple specification of  $A(R)$  is

$$A(R) \sim \delta(R) \quad (34)$$

However, we prefer to use a model  $A(R)$  with a somewhat extended support, which can be generalized to higher dimensions. We also want to retain a realistic mesoscopic nature of the reactive interaction for large  $\Omega$  (and increasing number density). If we scaled all Fourier components  $\hat{A}(k)$  like  $\hat{A}(0)$ , every particle would have a large number (of order  $\Omega$ ) of possible reaction partners at any one time but, with each of them, only a very small chance to react.

In order to keep the macroscopic features of the system constant on a macroscopic length scale and the mesoscopic nature of the processes constant on the mesoscopic length scale, we scale

$$A(R) = \bar{A}(R/l) \quad (35)$$

where  $l$  is a typical mesoscopic length and  $\bar{A}(x)$  is a scale-invariant<sup>9</sup> function. For  $l$  we specify the average nearest neighbor distance between reactants if their mass density equals the stationary value from the hydrodynamic equation and if they are distributed without spatial correlation:

$$l = m/\rho_s = \Omega^{-1}\bar{l}, \quad \rho_s = \lim_{D \rightarrow \infty} (b/a)^{1/2} \quad (36)$$

$\bar{l}$  is a macroscopic length related to the volume of 1 mole of substance X in a stationary system in the limit of infinitely fast diffusion. The function  $\bar{A}(x)$  is a hydrodynamic parameter, which in principle can be measured macroscopically, e.g., via the dependence of the reaction rate on the diffusion constant, even though this may be experimentally difficult because  $\bar{A}(x)$  still depends on the velocity persistence length, the temperature, the

<sup>9</sup> According to the periodic boundary conditions chosen,  $A(R)$  must be periodic with period  $2L$  in (10). Strictly, the function  $\bar{A}(x)$  must not depend on the system size and therefore cannot be periodic. So the scaling (35) can apply only for  $-L < R < L$ . Although this is obvious, the corresponding explicit notation is awkward and unnecessarily so because we are only interested in the case that the distance between reacting particles and also the distance between neighbor particles are much smaller than the system size. It is only to ease the notation that we extend  $\bar{A}(x)$  periodically by  $\bar{A}(x + 2L/l) = \bar{A}(x)$ . All integrations are understood to be performed over one period.



volume fraction of the reactants, etc.<sup>10</sup> In the limit  $D \rightarrow \infty$  the reaction rate constant  $a$  is related to  $\bar{A}(x)$  by

$$\lim_{D \rightarrow \infty} a = \hat{A}_0 l/m = \hat{A}_0 \bar{l}/\bar{m} \tag{37}$$

where  $\hat{A}_k$  is the Fourier transform of the single central peak of  $\bar{A}(x)$ :

$$\hat{A}_k = \int dx e^{ikx} \bar{A}(x) = \frac{2L}{l} \hat{A}(k/l)$$

One easily verifies that in the limit  $D \rightarrow \infty$  our Avogadro scaling

$$m = \Omega^{-1} \bar{m}\phi, \quad l = \Omega^{-1} \bar{l}, \quad L = \bar{L} \tag{38}$$

is equivalent to the system-size scaling

$$m = \bar{m}, \quad l = \bar{l}, \quad L = \Omega \bar{L} \tag{39}$$

(both  $\bar{m}$  and  $\bar{L}$  are scale-invariant and  $\Omega$  is dimensionless). Equation (28) with the scaling made explicit reads in both cases

$$SRK_0 SG = \frac{1}{2} \hat{A}_0 (\bar{l}/2\bar{L}\Omega) [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG + 2\bar{L}\Omega b/\bar{m} [\hat{x}(0) - 1] SG \tag{40}$$

where a factor  $\Omega^2$  is hidden in the second derivative  $\partial_{\hat{x}(0)}^2 SG$  because, e.g.,

$$\partial_{\hat{x}(0)}^2 SG|_{\hat{x}(0)=0} = \langle N(N-1) \rangle \tag{41}$$

and  $N$  scales linearly with  $\Omega$ .

However, the equivalence between (36) and (37) does not hold for the first-order correction in  $1/D$ , Eq. (31). This correction diverges for  $\Omega \rightarrow \infty$  in the system-size scaling because it follows from (31) that

$$SRK_1 SB = - \sum_{n=1}^{\infty} \frac{l^2}{8D\pi^2 n^2} \hat{A}_{k(n)}^2 [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG \tag{42}$$

where

$$k(n) = (l\pi/L)n \tag{43}$$

<sup>10</sup> Further examples of relevant macroscopically measurable quantities that we want to keep scale-invariant are the volume fraction of reactants, their mass concentration, and their specific weight. In particular, the limit  $\Omega \rightarrow \infty$  differs from the Grad limit that is used to derive the Boltzmann equation for hard spheres. There the total surface area of all spheres is kept constant and the volume fraction approaches zero. The total surface area of all reactants has no particular macroscopic interpretation in our case and its divergence in the limit  $\Omega \rightarrow \infty$  seems to be irrelevant.

For the system-size scaling (39), this is one order higher<sup>11</sup> in  $\Omega$  than the recombination term in (40). In contrast, in our Avogador scaling (38) the correction becomes somewhat insignificant because it is one order lower in  $\Omega$  than (40). Before we proceed with the explicit  $\Omega$ -expansion, we remark that (40) and (42) together with (44) ameliorate the deficit of the master Eq. (3) mentioned in the introduction in connection with cell models. The coefficient of the recombination term is now specified up to relative order  $\Omega^{-1}$  beyond the leading contribution by

$$a = a^{(0)} + a^{(1)}\Omega^{-1} + O(1/D^2, \Omega^{-2}) \tag{44}$$

where

$$a^{(0)} = \hat{A}_0 \bar{l} / \bar{m} \tag{45}$$

and

$$a^{(1)} = - \sum_{n=1}^{\infty} \frac{\bar{l}^2}{4D\pi^2 n^2} \frac{2\bar{L}}{\bar{m}} \hat{A}_{k(n)}^2$$

We summarize now the explicit substitutions of the  $\Omega$ -expansion for our case. They are closely analogous to the detailed treatment in Ref. 2 of the case of infinitely fast diffusion. The independent variable  $N$  in (3) is changed to the scaled continuous variable  $\xi$  by

$$N = (2\bar{L}/\bar{m})[\Omega\phi(t) + \Omega^{1/2}\xi], \quad P(N, t) = \Pi(\xi, t) \tag{46}$$

where the function  $\phi(t)$  will be defined presently. In particular, the step operators are represented by a Taylor expansion with respect to  $\xi$ :

$$\mathbb{E}P(N, t) = \left( \exp \frac{\bar{m}0^{-1/2}}{2\bar{L}} \partial_{\xi} \right) \Pi(\xi, t) \tag{47}$$

The highest order in  $\Omega$  that occurs in the resulting dynamic equation for  $\Pi$  is  $\Omega^{1/2}$ . All terms cancel in this order if  $\phi(t)$  obeys the equation

$$\partial_t \phi = b - a^{(0)}\phi^2 \tag{48}$$

This is the same equation as (2) in the limit  $\Omega \rightarrow \infty$ ; moreover, all centered moments of  $\Pi$  turn out to be of nonpositive order in  $\Omega$ , so  $\phi(t)$  gives the dominating contribution to the mass density for  $\Omega \rightarrow \infty$ , as it is evident from (46). So the hydrodynamic limit  $\Omega \rightarrow \infty$  is not affected in first order

<sup>11</sup> Strictly, we also have to account for an  $\Omega$  dependence of  $\hat{A}_{k(n)}$  because  $k(n) = \Omega^{-1} \bar{l} n / \bar{L}$ . However, this scaling depends on the explicit form of the function  $\bar{A}(x)$  and it is the same for both the system size and our Avogadro scaling. Any realistic  $\bar{A}(x)$  is sharply peaked at  $x = 0$  with a support much smaller than the interval  $[-1, +1]$ . So  $\hat{A}_k$  differs appreciably from  $\hat{A}_0$  only for  $k \gg 1$  for  $n \gg L/\bar{l}$ . These summands contribute very little to the sum in (42) because of the  $n^2$  dependence in the denominator. However, this is a peculiarity of our one-dimensional system and in higher dimensions the convergence of the sum depends crucially on the  $\lim_{n \rightarrow \infty} n^{d-2} \hat{A}_{k(n)}^2 = 0$ .

of  $1/D$ . The same is true of the next order in  $\Omega^{-1/2}$ , namely  $\Omega^0$ , where  $\Pi$  is found to obey the Fokker–Planck equation:

$$\partial_t \Pi(\xi, t) = \frac{1}{2} (b + 2a^{(0)}\phi^2) \frac{\bar{m}}{2L} \partial_\xi^2 \Pi + 2a^{(0)}\phi \partial_\xi \xi \Pi \tag{49}$$

The first-order effect of finitely fast diffusion is felt only from order  $\Omega^{-1/2}$  of the dynamic equation for  $\Pi$ . The notation is heavy at this level and to save writing, we change from the quantities  $\Omega$ ,  $\xi$ , and  $t$  to the following dimensionless ones<sup>12</sup>:

$$\begin{aligned} \Theta &= (a^{(0)})^{1/2} b^{1/2} t \\ \eta &= (\bar{m}/2L)^{-1/2} \rho_s^{-1/2} \xi \\ \omega &= (\bar{m}/2L)^{1/2} \rho_s^{-1/2} \Omega^{-1/2} \\ \alpha &= (a^{(1)}/a^{(0)}) \rho_s (\bar{m}/2L)^{-1} \end{aligned} \tag{50}$$

Also, we restrict ourselves to the stationary macroscopic state, i.e.,  $\phi(t) = (b/a^{(0)})^{1/2}$ .

The dynamic equation for  $\Pi$  is then, up to second order in  $\omega$ ,

$$\partial_\Theta \Pi = \frac{1}{4\omega^2} (1 + \alpha\omega^2)(e^{2\omega\partial_\eta} - 1)(1 + \omega\eta)(1 + \omega\eta - \omega^2)\Pi + \frac{1}{2\omega^2} (e^{-\omega\partial_\eta} - 1)\Pi \tag{51}$$

The approximation solution is easiest to obtain in terms of the moments  $\langle \eta^\nu \rangle$  of  $\Pi$ . The dynamic equations for them follow directly from (51):

$$\begin{aligned} \partial_\Theta \langle \eta \rangle &= \frac{\omega}{2} (1 - \alpha) + \left[ -1 + \omega^2 \left( \frac{1}{2} - \alpha \right) \right] \langle \eta \rangle - \frac{1}{2} \omega \langle \eta^2 \rangle + O(\omega^3) \\ \partial_\Theta \langle \eta^2 \rangle &= \frac{3}{2} - \omega^2 (1 - \alpha) + \omega (3 - \alpha) \langle \eta \rangle \\ &\quad + [-2 + 2\omega^2 (1 - \alpha)] \langle \eta^2 \rangle - \omega \langle \eta^3 \rangle + O(\omega^3) \\ \partial_\Theta \langle \eta^3 \rangle &= -\frac{3}{2} \omega + \left[ \frac{9}{2} - \omega^2 (7 - 3\alpha) \right] \langle \eta \rangle + \frac{3}{2} \omega (5 - \alpha) \langle \eta^2 \rangle \\ &\quad - \omega^2 (7 - 3\alpha) + \left[ -3 + 3\omega^2 \left( \frac{3}{2} - \alpha \right) \right] \langle \eta^3 \rangle - \frac{3}{2} \omega \langle \eta^4 \rangle + O(\omega^3) \\ \partial_\Theta \langle \eta^4 \rangle &= \frac{9}{2} \omega^2 - 6\omega \langle \eta \rangle + [9 + \omega^2 (-22 + 6\alpha)] \langle \eta^2 \rangle + 2\omega (7 - \alpha) \langle \eta^3 \rangle \\ &\quad + [-4 + 4\omega^2 (2 - \alpha)] \langle \eta^4 \rangle - 2\omega \langle \eta^5 \rangle + O(\omega^3) \\ \partial_\Theta \langle \eta^5 \rangle &= 15 \langle \eta^3 \rangle - 5 \langle \eta^5 \rangle + O(\omega) \end{aligned} \tag{52}$$

<sup>12</sup> The first three rescalings are closely analogous to Ref. 2, where this order in  $\Omega$  is discussed for a system with slightly different reactions in the limit  $D \rightarrow \infty$ . Note that  $\varepsilon$  in Ref. 2 is  $\omega$  here.

Fortunately, in the equation for every moment there occurs only one higher moment, namely the next higher one, and it carries a coefficient  $\omega$ . So in zeroth order in  $\omega$  one can solve for the subset of the first  $\nu$  consecutive moments. Also, all moments approach a finite stationary value in time, and the convergence for  $\omega \rightarrow 0$  is uniform with respect to  $\theta$ . One can now substitute the zeroth order of the moments  $\langle \eta \rangle \cdots \langle \eta^\nu \rangle$  on the right-hand side of (52) as coefficients of  $\omega$  and solve the first  $\nu - 1$  equations up to first order in  $\omega$ . After  $\mu$  iterations of this scheme one obtains  $\langle \eta \rangle \cdots \langle \eta^{\nu-\mu} \rangle$  up to  $\mu$ th order in  $\omega$ .

We give only two quantities that result from this calculation:

1. The average value of the fluctuation is

$$\langle \eta \rangle = \omega \left( \frac{1}{8} - \frac{1}{2} \alpha \right) + O(\omega^3) \quad (53)$$

2. The time-dependent autocorrelation function is

$$\begin{aligned} \langle \eta(\tau) \eta(\tau + \theta) \rangle &= \langle \eta^2 \rangle^2 (1 - e^{-\gamma\theta}) + \langle \eta^2 \rangle \left[ \left( \frac{1}{4} - \frac{1}{2} \alpha \right) e^{-\gamma\theta} + \left( \frac{3}{4} + \frac{1}{2} \alpha \right) e^{-\theta} \right] \\ &\quad - \frac{1}{2} \omega^2 (e^{-\gamma\theta} - e^{-2\theta}) + O(\omega^3, \epsilon^2) \end{aligned} \quad (54)$$

where

$$\langle \eta^2 \rangle = \frac{3}{4} + \frac{1}{2} \omega^2 (5/32 - \alpha), \quad \gamma = 1 + \omega^2 (\alpha - \frac{1}{2}) \quad (55)$$

## 6. DISCUSSION OF THE FIRST-ORDER CORRECTION $\epsilon^1$

If the master equation for a homogeneous (well-stirred) system like (3) is written in terms of the generating function, every reaction term is of the general form<sup>(8)</sup>

$$+ \text{const} \times (p_{\text{out}} - p_{\text{in}}) \partial_{\text{in}} G \quad (56)$$

$p_{\text{in}}$  and  $p_{\text{out}}$  denote the products of the generating variables for the occupation numbers of the ingoing and outgoing substances of the reaction and  $\partial_{\text{in}}$  is the product of partial derivative operators with respect to the generating variables for the ingoing substances. An example for this is the notation (28) for the right-hand side of (3).

The first-order correction term (31) contains two consecutive reaction operators. This resembles the virial expansion for an imperfect gas, where the first correction to the ideal gas limit arises from interactions between isolated pairs of particles. Here the first correction to the well-stirred limit arises from interdependence of isolated pairs of successive reaction (1b) events.

The functional dependence of (31) on  $\hat{x}(0)$  is the same as in the corresponding term of the zeroth order (28). This is because correlations between positions of pairs arise only from reactions in which there occur

more than one ingoing and one outgoing reactant. Also, only such reactions are sensitive to correlations that are at least bimolecular, e.g., the particle creation (1a) does not depend on correlations, nor does it give raise to any and the corresponding operator does not occur in (31).

The minus sign of (31) shows that the reaction (1b) is slowed down. This contradicts what one would expect if one ignored the subtle conceptual difference of  $\rho$  in (2) and (4). One could then reinterpret  $\rho(\mathbf{r}, t)$  as a fluctuating quantity and supplement (4) with a stochastic "Langevin" term. In "Langevin" diction, one describes the distortion of the spatial uniformity of  $\rho$  due to a single reaction event by a space-dependent fluctuation  $\delta\rho(\mathbf{r}, t)$  that has zero average when averaged over the volume of the system.<sup>(8)</sup> The correction due to imperfect partial equilibrium when the next reaction event occurs is then

$$-\left[ \int dr a(\rho + \delta\rho)^2 - \int dr a\rho^2 \right] = - \int dr a(\delta\rho)^2 \quad (57)$$

and the reaction (1b) appears to be accelerated—contrary to our result (31). The flaw with this argument is that it uses two microscopically different meanings for the macroscopically unique quantity "density." The quantity that obeys (4) even on the microscopic scale is a probability density that does not fluctuate. Its Fourier components are fast variables that go to a limit in partial equilibrium. On the contrary, fluctuations do occur in the microscopic distribution of X mass in the system. On the macroscopic scale the Fourier components of both quantities coincide and on a somewhat smaller length scale where the fluctuations are still small, the linear regression hypothesis can be used. On our length scale of interest, where single reactants are resolved, the fluctuations of the microscopic mass distribution are not small and in particular a fluctuation expansion<sup>(14)</sup> would not make sense.

The correct explanation for the minus sign in (31) is that in partial equilibrium (SG) the reactants are positioned independently from each other. This absence of correlations does not, of course, mean absence of fluctuations, i.e., at some places the reactants happen to be closer to each other than at other places. Starting from this partial equilibrium, a reaction (1b) event is most likely to occur between reactants that are close and thereafter the distribution of the remaining reactants RSG is more homogeneous in space than in the random partial equilibrium configuration. So the probability for a following reaction event is decreased. Obviously the contributions from small  $k$  values are particularly important because they decay least during the time between successive reaction events. This explains the factor  $T^{-1}$ , namely  $(-Dk^2)^{-1}$ , in (31). Also, those very high  $k$  values contribute little that correspond to wavelengths smaller

than the typical distance between reactants at the moment of reaction. Correlations on such a small length scale neither arise from a reaction event, nor do they change the probability for a successive one. This explains the factor  $\hat{A}^2(k)$  in (31).

A better pendant to which one can compare our expansion is the cluster expansion for diffusion-controlled reactions.<sup>(3,4,14,15)</sup> In its lowest order (Smoluchowski–Noyes theory) beyond the neglect of all correlations one considers pairs of reactants. This corresponds to the fact that the functional *RSG* to the right of  $T^{-1}$  in (31) is of second order in  $\hat{x}(k)$ . However, the higher orders of the cluster expansion—for which there exist no systematic results—differ from the higher orders in our scheme.

In particular, the cluster expansion amounts to a Taylor expansion of the logarithm of the functional  $G$  for an infinite system around the point  $x(r) \equiv 1$  in function space:

$\log G(\{x(r)\}, t)$

$$= \sum_{n=1}^{\infty} \frac{1}{n!} \int dr_1 \cdots dr_n [x(r_1) - 1] \cdots [x(r_n) - 1] g_n(r_1, \dots, r_n, t) \quad (58)$$

One then obtains from (10) a hierarchy of dynamical equations for the functions  $g_n$  that describe correlation between clusters of  $n$  reactants. Successively higher functions  $g_n$  turn out to be of successively higher order in  $A(r)$ . Small values for  $A(r)$  mean that the reactant pair distribution is only little depleted for small mutual distances and that diffusion can destroy the arising pair correlations relatively fast.

The cluster expansion agrees with the adiabatic elimination in that the first-order correction can be derived from the exact solution of the two-reactant problem, i.e., for the case that  $G$  contains no higher powers of  $\hat{x}(0)$  than second. The exact solution for a system with two particles is equivalent to the problem of finding a closed form for the right-hand side of (26) after one has dropped all higher derivatives than the second. This reproduces the first-order (31) correctly. Also, this solution amounts to the solution of the dynamic equation for  $g_2$  and neglecting  $g_3$ . However, in the next order in the cluster expansion there appear three-particle correlations, while our scheme accounts for correlations between three reaction events, which turn out to contribute in fourth order in the number of reactants in the system.

The expansions differ also in that the Smoluchowski–Noyes theory, in its customary form, deals with a system of infinite extent. It ignores the slow long-range fluctuations, whereas (31) ascribes a large effect to the smallest  $k$ -values that the system can accommodate. The reason for this relative shortcoming of the cluster expansion is twofold. When it is applied

to a time-dependent situation, it is common to consider the initial condition that the system is well-stirred and the reactant positions are completely uncorrelated. The slow long-range fluctuations take a long time to develop and are small during the short-time regime, so that the cluster expansion adequately describes the situation. When it is applied to a system in the stationary state, the cluster expansion still ignores the correlations that arise from large clusters. The importance of these correlations for the approach to the stationary state is evident from the divergence of the higher order terms in (3.13) in the limit of infinite system-size. It is also evident that these higher order terms are of higher order in  $A(r)$ , so they correspond to high orders in the cluster expansion.

The correct application of the  $\Omega$ -expansion to our system shows that the hydrodynamic Eq. (2) is not affected in order  $\varepsilon^1$  and neither are the fluctuations in the linear noise approximation. Fluctuation effects beyond this order in  $\Omega^{-1/2}$  are unmeasurably small in order  $\varepsilon^0$ . In order  $\varepsilon^1$  we find the average mass density in the stationary state to be

$$\langle \rho \rangle = \frac{m}{2L} \langle N \rangle = \rho_s \left( 1 - \frac{1}{2} a^{(1)} \frac{\Omega^{-1}}{a_{(0)}} \right) + \frac{1}{8} \frac{m}{2L} + O(\Omega^{-2}, \varepsilon^2) \quad (59)$$

where

$$\begin{aligned} a^{(0)} &= \lim_{\varepsilon \rightarrow 0} a = \frac{1}{m} \int dr A(r) \\ a^{(1)} \Omega^{-1} &= -\frac{m}{2L} \sum_{n=1}^{\infty} (D\pi^2 n^2)^{-1} \left( \int dr A(r) \cos \frac{n\pi r}{L} \right)^2 \\ \rho_s &= (b/a^{(0)})^{1/2} \end{aligned}$$

The deviation from the hydrodynamic value  $\rho_s$  amounts in order  $\varepsilon^0$  only to one-eighth of a single reactant molecule in the whole system. On the contrary, it is not small for large systems in order  $\varepsilon^1$ . For large  $L$ , the cosine in the expression for  $a^{(1)} \Omega^{-1}$  can be safely replaced by unity because the convergence of the sum is ensured by the factor  $1/n^2$ . With help of the identity

$$\sum_{n=1}^{\infty} n^{-2} = \pi^2/6 \quad (60)$$

the relative deviation  $(\langle \rho \rangle - \rho_s)/\rho_s$  is obtained for large  $L$  [much larger than the support of  $A(r)$ ] as

$$-\frac{1}{2} a^{(1)} \Omega^{-1} / a^{(0)} = a^{(0)} m 2L / 12D + O(L^0) \quad (61)$$

This shift of the average density from the hydrodynamic value  $\rho_s$  is caused by correlations between reactant positions; however, the fluctuations of the

density around this shifted average show no pronounced dependence on  $D$ , and the equal-time autocorrelation of the density changes only according to the increase in the average value:

$$\langle\langle \rho^2 \rangle\rangle = \langle \rho^2 \rangle - \langle \rho \rangle^2 = \frac{m}{2L} \left( \frac{3}{4} \langle \rho \rangle - \frac{1}{32} \frac{m}{2L} \right) + O(\Omega^{-5/2}, \epsilon^2) \quad (62)$$

Another typical effect in the second order of the  $\Omega$ -expansion is that there occur multiple decay constants in the time-dependent autocorrelation of the density. This effect does not change in order  $\epsilon^1$ , as is evident from the results of the previous section. So the only effect of the  $\epsilon^1$  correction on the density is accounted for by a renormalization of the rate constant for the process (1b):

$$\langle \rho \rangle = \left( \frac{b}{a} \right)^{1/2} + \frac{1}{8} \frac{m}{2L} + O(\Omega^{-2}, \epsilon^2) \quad (63)$$

where  $a = a^{(0)} + a^{(1)}\Omega^{-1} + O(\Omega^{-2})$ .

### 7. DISCUSSION OF THE CORRECTION IN ORDER $\epsilon^2$

The first sum in (32) has the same functional dependence on  $\hat{x}(0)$  as the first-order correction (31) and its effect is a similar renormalization of the rate constant for the recombination process. The rate constant is then defined up to second order in  $\Omega^{-2}$ , so

$$a = a^{(0)} + a^{(1)}\Omega^{-1} + a_1^{(2)}\Omega^{-2} + \dots \quad (64)$$

where now

$$a_1^{(2)}\Omega^{-2} = \left( \frac{m}{2L} \right)^{-1} \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{1}{4D^2 k_1^2 k_2^2} \hat{A}(k_1) \hat{A}(k_1 + k_2) \hat{A}(k_2) \quad (65)$$

As in the first order, the convergence of the sums is ensured by the inverse squares of the summation indices, and for large systems the  $k$  values are so closely spaced on the scale on which  $\hat{A}(k)$  varies that one can approximate  $\hat{A}(k)$  by  $a^{(0)} m/2L$ , so

$$a_1^{(2)}\Omega^{-2} = \frac{(a^{(0)})^3 L^2 m^2}{144 D^2} + O(L) \quad (66)$$

As a new feature in (32) there occur fourth-order derivatives with respect to  $\hat{x}(0)$  in the second sum and also a combination of jump rate constants for different processes in the third sum. Both are due to the embedded projection operator  $S$  in  $SRT^{-2}FRSRSG$ .



The dependence of the second sum on  $\hat{x}(0)$  does not match the pattern (56), but it can be split uniquely into parts that do match:

$$\begin{aligned}
 & - [1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 [1 - \hat{x}(0)] \partial_{\hat{x}(0)}^2 SG \\
 & = 2[\hat{x}^2(0) - \hat{x}(0)] \partial_{\hat{x}(0)}^4 SG - [1 - \hat{x}^4(0)] \partial_{\hat{x}(0)}^4 SG \\
 & \quad + 4[\hat{x}^2(0) - \hat{x}^3(0)] \partial_{\hat{x}(0)}^3 SG + 2[1 - \hat{x}^2(0)] \partial_{\hat{x}(0)}^2 SG \quad (67)
 \end{aligned}$$

So this part of the  $\varepsilon^2$  correction can be interpreted as four concurrent reaction processes, namely



These virtual processes appear to occur concurrently, independently from each other. Only the probability rates at which the events occur are related to the same parameter combination and they cannot be varied separately.

The negative probability rate in the second term in (67) resembles the negative  $\varepsilon^1$  correction, but here there is no lower order process to be slowed down. As the  $\Omega$ -expansion shows, the major effect is a narrowing of the density fluctuations. The interpretation of the third sum is very similar to this.

An estimate of the dominant effects in order  $\varepsilon^2$  is provided by the  $\Omega$ -expansion of (32). To apply it, we make the  $\Omega$ -scaling explicit and translate back to the master equation in number space (3a). The first sum contributes only in order  $\Omega^{-2}$ , but the second and the third sums contribute in order  $\Omega^0$ , i.e., at the linear noise level. They are

$$\begin{aligned}
 & + \sum_{n=1}^{\infty} \frac{L^3}{8D^2\pi^4 n^4} \hat{A}_{k(n)}^2 \hat{A}_0 \Omega^{-3} (\mathbb{E}^2 - 1) \binom{N}{2} (\mathbb{E}^2 - 1) \binom{N}{2} P(N, t) \\
 & \quad + \sum_{n=1}^{\infty} \frac{L^4}{2D^2\pi^4 n^4} \hat{A}_{k(n)}^2 a^{(0)} \frac{\bar{m}}{2L} \Omega^{-1} (\mathbb{E}^2 - 1) \binom{N}{2} (\mathbb{E}^{-1} - 1) P(N, t) \quad (69)
 \end{aligned}$$

The factors  $N$  are of order  $\Omega$  and every  $(\mathbb{E}^v - 1)$  operator contributes a factor  $\Omega^{-1/2}$ .

The result for the average density in the stationary state is

$$\langle \rho \rangle = \left(\frac{b}{a}\right)^{1/2} + \frac{m}{2L} \left(\frac{1}{8} - \frac{1}{4} c\right) + O(\Omega^{-2}, \varepsilon^3) \quad (70)$$

and the time-dependent autocorrelation is

$$\langle \rho(0) \rho(t) \rangle - \langle \rho(0) \rangle^2 = \frac{3}{4} \rho_s \frac{m}{2L} \left( 1 - \frac{4}{3} c \right) e^{-2a\rho_s t} + O(\Omega^{-2}, \varepsilon^3) \quad (71)$$

where

$$c = \sum_{n=1}^{\infty} \frac{L^4}{D^2 \pi^4 n^4} \hat{A}_{k(n)}^2 \approx \frac{L^4}{90D^2} a^{(0)} b$$

Again for large system size we have substituted  $(a^{(0)}b)^{1/2}$  for  $\hat{A}_{k(n)}$  and we have used  $\sum_{n=1}^{\infty} n^{-4} = \pi^4/90$ .

Evidently, the  $\varepsilon^2$  corrections have effects at the linear noise level of the  $\Omega$ -expansion, i.e., at leading order of  $\langle \rho^2 \rangle - \langle \rho \rangle^2$  in  $\Omega^{-1/2}$ , whereas the  $\varepsilon$  correction (31) contributes only one order higher in  $\Omega^{-1/2}$ . This is due to the final factor  $SRS$  in the operator string working on  $SG$  in the second and third sums of (32). The operator  $SRS$  is of order  $\Omega^{1/2}$ , as we know already from the  $\varepsilon^0$  contribution (28), and the order of the other operator part, which occurs to the left of it, is  $\Omega^{-1/2}$ , similar to the  $\varepsilon$  contribution (31).

Inspection of the analogous term (27a) at general order  $n$  shows that it is of order  $\Omega^{(n-2)/2}$ , because the part  $SRT^{-n}FRS$  is invariably of order  $\Omega^{-1/2}$  for all  $n \geq 1$ . So from order  $\varepsilon^3$  on we expect changes in the hydrodynamic equation (order  $\Omega^{1/2}$ ) and for still higher orders in  $\varepsilon$  the limit  $\Omega \rightarrow \infty$  no longer exists.

In the present form of the  $\Omega$ -expansion the limits  $\varepsilon \rightarrow 0$  and  $\Omega \rightarrow \infty$  have to be taken so that  $\varepsilon\Omega^{1/2} \ll 1$ . The physical regime where this restriction is met is best characterized in terms of the time scales of the problem:

1. The diffusion time  $\tau_D$ , namely the decay time of the slowest transport mode:

$$\tau_D = 4D^{-1}L^2 \sim \varepsilon^1 \Omega^0 \quad (72)$$

2. The macroscopic reaction time  $\tau_R$ , namely the decay time of the autocorrelation of the total number of reactants in a well-stirred system in the steady state:

$$\tau_R = \frac{1}{2} a^{-1/2} b^{-1/2} \sim \varepsilon^0 \Omega^0 \quad (73)$$

This time is half of the average lifetime of a particle in our example.

3. The microscopic reaction time  $\tau'_R$ , namely the average time between successive annihilation events in the stationary state:

$$\tau'_R = m/Lb \sim \varepsilon^0 \Omega^{-1} \quad (74)$$

This is the time scale for the process that *generates* the correlations between the particle positions and that is sensitive to them.

Our treatment requires

$$\tau_D \ll (\tau_R \tau'_R)^{1/2} \quad (75)$$

or else we would have to resum because the corrections to (2) become large.

This result is more restrictive than the requirement that the average particle must have time to move through the whole volume of the system during its lifetime:  $\tau_D \ll \tau_R$ , which amounts only to  $\varepsilon \ll 1$ .

## 8. HIGHER DIMENSIONS

The generalization to  $d$  dimensions of the dynamical equation for the functional (10) and the Fourier transformation is a mere change in the dimension of the integrals and the normalization constants. In the correction terms the sums over  $k$  values must be extended so that  $k$  assumes all values  $((\pi/L)n_1, \dots, (\pi/L)n_d)$ , where  $n_1, \dots, n_d$  are integers. The scaling with  $\Omega$  changes only in that more generally  $\bar{l} = (\bar{m}/\rho_s)^{1/d}$ , and all  $\hat{A}(k)$  remain of the same order  $\Omega^{-1}$ .

The major difference for  $d > 1$  is that the convergence of the sums over  $k$  can no longer rely on the factors  $k^{-2n}$  from  $T^{-n}$ , because the number of terms in a certain interval of  $|k|$  values  $[|k|, |k| + \Delta]$  is proportional to  $|k|^{d-1}$ . A sufficient condition for convergence, which is met by all physically reasonable models for  $\hat{A}(k)$ , is that

$$\hat{A}(k) \sim O(|k|^{1-d}) \quad \text{for } k \rightarrow \infty$$

In the respective sums, the slow, long-ranged transport modes lose importance in higher dimensions because they are relatively few.

## 9. CONCLUDING REMARKS

The main achievement of this paper is the systematic deduction of a reduced macroscopic description from the mesoscopic  $N$ -body level for a one-dimensional diffusion reaction system. The preexisting tools for this are the adiabatic elimination procedure, which goes back to Block's variant of degenerate perturbation theory,<sup>(13,16)</sup> and van Kampen's  $\Omega$ -expansion.<sup>(2)</sup> Both were applied for the first time systematically to a diffusion reaction system in continuous space. In particular, we avoided any unsystematic cell model description with macroscopic, homogeneous cells. Our new form of

the  $\Omega$ -expansion, namely the Avogadro scaling, applies also to the case of diffusion-controlled reactions, where the correlations between reactant positions are not small.

The main conceptual result of this paper is the explicit restriction (75) under which (2) is a valid approximation. Contrary to modern textbooks,<sup>(2,8)</sup> this length is not the macroscopic "Kuramoto"<sup>(5,17)</sup> length  $(\tau_R/D)^{1/2}$ , namely the average distance that a reactant particle travels by diffusion during its lifetime. Rather, the semimicroscopic length  $\tau_R^{1/4}\tau_R^{1/4}D^{-1/2}$  is the upper limit. It goes to zero like  $\Omega^{-1/5}$  in the thermodynamic limit, so that the average number of particles in the system in the steady state goes to infinity like  $\Omega^{4/5}$ .

Our form of the adiabatic elimination resembles two other methods, namely the cluster expansion for diffusion reaction systems<sup>(4)</sup> and the Chapman-Enskog treatment of the linearized Boltzmann equation for fluids, which we discuss in turn.

The various orders of the cluster expansion describe the correlations between clusters of reactants, i.e., the  $n$ -cluster term is of order  $(n-1)$  in the reaction probability of encountering reactants. The cluster expansion retains the details of the two-particle interaction, but it also has two drawbacks in comparison with our method: (1) there is no exact explicit result available for three-particle and higher correlations; (2) for some reactions it is clearly not valid outside the steady state and for long times.<sup>(18)</sup> It is not apparent when it does fail and when not. Our adiabatic elimination avoids the details of the correlations between clusters of  $n$  particles, although this detail can be reconstructed easily from the solution for the time after the initial transient regime. The various orders describe the interaction between successive reaction events and even the higher orders are straightforward to compute. It is made to describe the long-time behavior.

The Chapman-Enskog procedure has been shown to correspond formally to Bloch's variant of degenerate perturbation theory.<sup>(16)</sup> It has been applied previously<sup>(6)</sup> to a cell model of the same chemical reactions as ours, and the results correspond to ours. On the physical side, however, the original Chapman-Enskog problem can be mapped to our problem in two different ways. As in our problem, Chapman-Enskog expand around a partial equilibrium which is attained because the collisions occur very frequently on the time scale of interest. However, in our problem there are two different sorts of collisions, namely collisions between reactants and the host medium particles and collisions between reactants.

The dominant collisions in our problem are the ones with the host medium particles, which are described by the diffusion term. The reactant-reactant collisions constitute the slow process in our case, which is not related to the slow process in the fluid problem, namely free motion

between collisions. In this analogy, our virtual reaction paths correspond to the Burnett and “super”-Burnett terms<sup>(16)</sup> found in the Chapman–Enskog problem.

The other analogy concerns the hierarchy of correlation functions in both cases.<sup>(3,4)</sup> Here the reactive collisions between reactants play a similar role to the collisions in the fluid case, because these are the mechanisms by which correlations between particles arise. The free diffusion of the reactions through the host medium then corresponds to the free motion of fluid molecules between collisions. In this respect, our adiabatic elimination is just the opposite of the Chapman–Enskog problem, because we assume that the free diffusion occurs rapidly. Interestingly, there is a physical regime where the free motion in a fluid dominates over the collisions, namely if the probing wavelength is small compared to the mean free path.<sup>(19)</sup> However, the adiabatic elimination in that case is more difficult, because the eigenvalues of the free streaming operator are purely imaginary and not large, real, and negative, as are those of the diffusion operator.

There remain two main drawbacks of our treatment in comparison to a full real-space renormalization of diffusion reaction systems,<sup>(20)</sup> which remains as an outstanding challenge:

1. We have eliminated all transport modes at once and the length of our coarse-graining is the size of the system.

For a selective elimination of fast transport modes with  $|k| > |k|_{\text{cutoff}}$ , one can no longer expand in inverse powers of  $D$ . The expansion parameter is then the quotient of the absolutely largest eigenvalue of the reaction operator  $SRS$  in the slow subspace and the decay constant  $Dk_{\text{cutoff}}^2$  of the slowest transport mode to be eliminated. The former eigenvalue is related to the fastest reaction process that is not eliminated. The lowest order of this modified scheme corresponds formally to the scheme in this article. However, the explicit computation of even the first-order correction requires the summation of the infinitely many terms of the form (27a), which proved most divergent in our secondary  $\Omega$ -expansion. Such a summation would constitute the crucial reduction step of a renormalization.

2. We have applied the  $\Omega$ -expansion on top of the adiabatic elimination in the slow subspace only and not directly to the dynamic equation for the  $G$  functional on the  $N$ -body level. This would be the scaling step of a renormalization and would overcome the restriction  $\varepsilon\Omega^{1/2} \ll 1$ .

We hope to come back to the mentioned shortcomings and extend our explicit results to higher dimensions in a future publication.

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