Journal of Statistical Physics, Vol. 49, Nos. 5/6, 1987

Fluctuations in Coagulating Systems. II

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Received May 18, 1987; revision received August 17, 1987

In this paper we consider coagulation processes in large but finite systems, and study the time-dependent behavior of the (nonequilibrium) fluctuations in the cluster size distribution. For this purpose we apply van Kampen's Ω-expansion to a master equation describing coagulation processes, and derive an approximate (Fokker–Planck) equation for the probability distribution of the fluctuations. First we consider two exactly soluble models, corresponding to the choices $K(i, j) = i + j$ and $K(i, j) = 1$ for the rate constants in the Fokker–Planck equation. For these models and monodisperse initial conditions we calculate the probability distribution of the fluctuations and the equal-time and two-time correlation functions. For general initial conditions we study the behavior of the fluctuations at large cluster sizes, and in the scaling limit. Next we consider, in general, homogeneous rate constants, with the property $K(i, j) = a^{-\lambda}K(ai, aj)$ for all $a > 0$, and we give asymptotic expressions for the equal-time correlation functions at large cluster sizes, and in the scaling limit. In the scaling limit we find that the fluctuations show relatively simple scaling behavior for all homogeneous rate constants $K(i, j)$.

KEY WORDS: Fluctuations; coagulation; Smoluchowski theory; scaling behavior.

1. INTRODUCTION

In this paper we continue our study[1] of the stochastic properties of the fluctuations in large but finite, spatially homogeneous coagulating systems. We consider two new, exactly soluble, nongelling models, where the properties of the fluctuations can be studied in great detail. The insight obtained from these exactly soluble models and from the gelling model considered in Ref. 1 then leads to approximate expressions, including a scaling theory, for the fluctuations in more general systems.

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0022-4715/87/1200-0927$05.00/0

Our method works as follows. We start from a master equation describing coagulating processes in finite, spatially homogeneous systems, and we assume that these systems are *large*. In most cases of interest, the master equation cannot be solved exactly. To obtain an *approximate* description of the fluctuations, valid if the system is large, we expand the master equation in powers of the inverse system size. This technique is known as the Ω-expansion.[2] In the expansion we retain only the first few terms. From the leading terms we recover the deterministic approach to coagulation processes (Smoluchowski theory), where the fluctuations are not taken into account. The next order yields an approximate (Fokker–Planck) description of the fluctuations that is much more tractable than the original master equation approach.

In the stochastic approach to coagulation processes[1,3–6] one considers a *finite system* of volume V containing M basic units, and one constructs a *master equation* for the probability $P(\mathbf{m}, t)$ that the number of k-mers, or clusters of size k, at time t is given by m_k ($k = 1, 2,...$). The possible states of the system are thus described by a vector $\mathbf{m} = (m_1, m_2,...)$. If the rate constants for the clustering of an i- and a j-mer are given by K_{ij}, then the master equation for $P(\mathbf{m}, t)$ reads

$$\dot{P}(\mathbf{m}, t) = (2V)^{-1} \sum_{i,j} K_{ij} \Delta_{ij}[m_i(m_j - \delta_{ij})\, P(\mathbf{m}, t)] \tag{1.1}$$

where δ_{ij} is a Kronecker delta, and Δ_{ij} is a difference operator. The action of Δ_{ij} is defined for an arbitrary function $f(\mathbf{m})$ as

$$\Delta_{ij} f(\mathbf{m}) = f(\{m_k + \delta_{ik} + \delta_{jk} - \delta_{i+j,k}\}) - f(\mathbf{m}) \tag{1.2}$$

In the right-hand side of (1.1) we distinguish a gain and a loss term, corresponding, respectively, to the first and second terms on the right in (1.2). The *gain term* represents all possible ways to reach the state $\mathbf{m}$ from states with an i-mer and a j-mer more and an $(i+j)$-mer less. The transition rates are $V^{-1}K_{ij}(m_i+1)(m_j+1)$ if $i \neq j$, and $V^{-1}K_{ii}(m_i+2)(m_i+1)$ if $i = j$. Similarly, the *loss term* represents all possible ways to leave the state $\mathbf{m}$. We remark that everywhere below we set the density equal to unity, i.e., we choose the unit of volume such that $M = V$.

An important property of the master equation (1.1), which plays a central role in this paper, is the *conservation law for the total mass*, i.e.,

$$\sum_k k m_k = M \tag{1.3}$$

Equation (1.3) simply states that the total number of units in the system is fixed and equal to M. As an immediate consequence one finds that clusters

of size $k > M$ cannot occur, i.e., that at all times $m_k = 0$ if $k > M$. Nevertheless, it is convenient to describe the system in terms of an *infinite* number of variables $\mathbf{m} = (m_1, m_2, \ldots)$, and let the summation indices in (1.1) and (1.3) run from one to infinity. The reason for this will become clear below.

In the limit of an *infinite system*, i.e., if $M \to \infty$, the fluctuations in m_k can be neglected, and the master equation (1.1) reduces to a kinetic equation for the k-mer concentrations $c_k(t)$ $(k = 1, 2, \ldots)$. More precisely, in the limit $M \to \infty$ the average number of k-mers increases proportional to the system size, $\langle m_k(t) \rangle \sim M c_k(t)$, where the concentration $c_k(t)$ satisfies the *macroscopic law*:

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \qquad (k = 1, 2, \ldots) \tag{1.4}$$

Equation (1.4) is known as Smoluchowski's coagulation equation.[7-9] The conservation law (1.3) for the total mass implies the following relation for the concentrations $c_k(t)$:

$$\sum_{k=1}^{\infty} k c_k(t) = 1 \tag{1.5}$$

This relation simply states that the mass density in the infinite system is equal to unity. Equation (1.5) can also be verified directly from (1.4).[2]

In *large* but *finite* systems, there will always be fluctuations around the average behavior, as described by (1.4). In order to study these fluctuations we use van Kampen's Ω-expansion,[2] which is an expansion of the master equation in powers of the inverse system size. In our case the system size is M. The basic idea of the Ω-expansion is that the fluctuations about the average behavior $\langle m_k \rangle$ are *small*, of the order of $M^{1/2}$. In this case we can transform from the original variables m_k in the master equation to new variables ξ_k defined by

$$m_k \equiv M c_k(t) + M^{1/2} \xi_k \qquad (k = 1, 2, \ldots) \tag{1.6}$$

where $c_k(t)$ is the solution of the macroscopic law (1.4). The assumption that the fluctuations are of the order of M then implies that the scale of ξ_k remains finite as $M \to \infty$. In the limit $M \to \infty$, the master equation (1.1) for $P(\mathbf{m}, t)$ reduces to a linear Fokker–Planck equation for the probability

[2] From Ref. 1 we know that the conservation law (1.5) breaks down in *gelling models* if, at some finite time t_c (gelpoint), there occurs a phase transition, and an "infinite" cluster, or gel, is formed. Such complications need not worry us here: in this paper we do *not* consider the post-gel stage $(t > t_c)$ of gelling models.

density $\Pi(\xi, t)$ that the fluctuations at time t have the value $\xi = (\xi_1, \xi_2, \ldots)$. The Fokker–Planck equation for $\Pi(\xi, t)$ is the starting point for our calculations in this paper.

The essence of our method, therefore, is, that we transform from m_k to new variables ξ_k, as in (1.6), and study the stochastic properties of ξ_k *in the infinite system*, i.e., in the limit $M \to \infty$. In an infinite system, however, all possible cluster sizes are allowed, requiring the use of an infinite number of variables ξ_k $(k = 1, 2, \ldots)$. As a consequence the *right*-hand side of (1.6) is defined for all $k \geqslant 1$. For this reason it is convenient to start from a master equation in terms of an infinite number of variables m_k, so that also the *left*-hand side of (1.6) is defined for all $k = 1, 2, \ldots$.

The bulk of this paper is devoted to two new, exactly soluble models, in which the properties of the fluctuations can be studied in full detail, at least within the Fokker–Planck approximation. The rate constants corresponding to these models are

$$K_{ij} = i + j \tag{1.7a}$$

and

$$K_{ij} = 1 \tag{1.7b}$$

The first model, $K_{ij} = i + j$, is a stylized version of the classical polymerization models $\mathrm{ARB_g}$ of Flory and Stockmayer,[10,11] which describe the growth of *branched* polymers. The second example, $K_{ij} = 1$, can be interpreted[12] as a model for the growth of *linear* polymers.

After discussing the exactly soluble models $K_{ij} = i + j$ and $K_{ij} = 1$, we use the insight obtained from these nongelling models and from the gelling model $K_{ij} = ij$ considered in Ref. 1 to study the fluctuations in *more general* coagulating systems. For this purpose we consider the large class of rate constants $K(i, j)$ that are *homogeneous* functions of the cluster sizes i and j, with the additional property that the behavior of $K(i, j)$ for $j \gg i$ is described by two exponents μ and ν, as follows:

$$K(ai, aj) = a^{\lambda} K(i, j) \qquad (\text{all } a > 0) \tag{1.8a}$$

$$K(i, j) \sim i^{\mu} j^{\nu} \qquad (j \gg i;\ \mu + \nu = \lambda) \tag{1.8b}$$

The form (1.8) for $K(i, j)$ is quite general. All kernels used in the literature[8,9] have the properties (1.8a), (1.8b) at least for large values of i and j. For physical reasons[13] the possible values of ν and λ are restricted to $\nu \leqslant 1$ and $\lambda \leqslant 2$. Furthermore, it is known[13] that an exponent $\lambda > 1$ leads to gelation, whereas for $\lambda \leqslant 1$ gelation does not occur. Note that the exactly soluble models are contained in (1.8) as special cases.

For the models $K_{ij} = i + j$ and $K_{ij} = 1$, the macroscopic law, i.e., Eq. (1.4), can be solved exactly[14–16] for general initial conditions $c_k(0)$ ($k = 1, 2, \ldots$). Some relevant results for the solutions $c_k(t)$ of (1.4) with rate constants $K_{ij} = i + j$ or $K_{ij} = 1$ are summarized in Appendix A. Much less is known concerning the solutions of the master equation with rate constants (1.7a) or (1.7b). In both models, the solution $P(\mathbf{m}, t)$ of the master equation (1.1) is known only for *monodisperse* initial conditions, i.e., if $m_k(0) = M\delta_{k1}$. The solution for $K_{ij} = i + j$ has been found by Lushnikov[5] and the case $K_{ij} = 1$ has been solved by Bayewitz *et al.*[4] For general initial conditions the solution of Eq. (1.1) is not known. Moreover, even for monodisperse initial conditions many interesting properties remain undetermined. Examples of such unknown quantities are the two-time correlation functions $\langle\langle m_i(t_1)\, m_j(t_2)\rangle\rangle$ and, for $K_{ij} = 1$, the average number of k-mers $\langle m_k \rangle$ and the equal-time correlation functions or covariances $\langle\langle m_i(t)\, m_j(t)\rangle\rangle$.

For homogeneous kernels, different from (1.7a), (1.7b) or $K_{ij} = ij$, neither the master equation nor the macroscopic law can be solved *exactly*. However, it is possible to study the *asymptotic* behavior of the solutions $c_k(t)$ of Smoluchowski's equation in various limits.[13,17,18] Some relevant results from the literature are given in Appendix A.

The plan of this paper is as follows. In Section 2 we discuss the Ω-expansion of the master equation and we derive equations for the averages and covariances of the fluctuations. Then we consider the *first* exactly soluble model, $K_{ij} = i + j$. Monodisperse initial conditions are the subject of Section 3, and general initial conditions that of Section 4. The *second* exactly soluble model, $K_{ij} = 1$, is treated in Section 5 for monodisperse initial conditions, and in Section 6 for general initial conditions. Section 7 is devoted to homogeneous kernels: the main result of this section is a *scaling theory* for the fluctuations in gelling and nongelling systems. In Section 8 we summarize and discuss our results. Relevant results from the literature are summarized in Appendix A. Appendix B is a technical appendix.

2. THE Ω-EXPANSION OF THE MASTER EQUATION

The basic idea of the Ω-expansion has been sketched around Eq. (1.6): we transform from the occupation numbers m_k in (1.1) to new variables ξ_k, and we replace the probability distribution $P(\mathbf{m}, t)$ with the probability distribution $\Pi(\xi, t)$ for the new variables $\xi = (\xi_1, \xi_2, \ldots)$. Two points require further attention, namely the transformation of the time derivative $\dot{P}(\mathbf{m}, t)$ in (1.1) and the transformation of Δ_{ij}. These points will be discussed next.

First we consider the transformation of the time derivative in (1.1). We

note that $\dot{P}(\mathbf{m}, t)$ is calculated with m_k constant. According to (1.6), constant m_k implies that

$$d\xi_k/dt = -M^{1/2}\dot{c}_k(t) \qquad (k = 1, 2, \ldots) \tag{2.1}$$

It follows that the time derivative $\dot{P}(\mathbf{m}, t)$, expressed in terms of the new variables ξ, assumes the form

$$\frac{\partial \Pi}{\partial t} + \sum_{k=1}^{\infty} \frac{\partial \Pi}{\partial \xi_k}\frac{d\xi_k}{dt} = \frac{\partial \Pi}{\partial t} - M^{1/2} \sum_{k=1}^{\infty} \dot{c}_k(t)\frac{\partial \Pi}{\partial \xi_k} \tag{2.2}$$

Second, the difference operator Δ_{ij} in (1.2) can be written as a differential operator in terms of the variables ξ_k:

$$\begin{aligned}\Delta_{ij} &= \exp\left[\sum_{k=1}^{\infty} (\delta_{ik} + \delta_{jk} - \delta_{i+j,k})\frac{\partial}{\partial m_k}\right] - 1 \\ &= \exp(M^{-1/2} D_{ij}) - 1\end{aligned} \tag{2.3a}$$

where D_{ij} is defined as

$$D_{ij} \equiv \sum_{k=1}^{\infty} (\delta_{ik} + \delta_{jk} - \delta_{i+j,k})\frac{\partial}{\partial \xi_k} \tag{2.3b}$$

For large values of the system size M, we can expand the exponential in (2.3a) in a Taylor series as follows:

$$\Delta_{ij} = M^{-1/2} D_{ij} + \tfrac{1}{2} M^{-1} (D_{ij})^2 + \cdots \qquad (M \to \infty) \tag{2.4}$$

For our purposes it suffices to take into account only the first two terms on the right in (2.4). The contributions of higher order terms are negligibly small as $M \to \infty$.

We are now in a position to carry out the expansion of the master equation (1.1) in powers of $M^{-1/2}$. Substitution into (1.1) of Eq. (1.6) for m_k and Eqs. (2.2) and (2.4) for $\dot{P}(\mathbf{m}, t)$ and Δ_{ij} yields the following result for the probability distribution $\Pi(\xi, t)$ as $M \to \infty$:

$$\begin{aligned}&\frac{\partial \Pi}{\partial t} - M^{1/2} \sum_{k=1}^{\infty} \dot{c}_k(t)\frac{\partial \Pi}{\partial \xi_k} \\ &\quad = M^{1/2}\left(\tfrac{1}{2}\sum_{i,j} K_{ij} c_i c_j D_{ij} \Pi\right) \\ &\qquad + \tfrac{1}{2}\sum_{i,j} K_{ij}[D_{ij}(c_i \xi_j + c_j \xi_i) + \tfrac{1}{2} c_i c_j (D_{ij})^2]\,\Pi + O(M^{-1/2})\end{aligned} \tag{2.5}$$

In the derivation of Eq. (2.5) we arranged the terms on the right-hand side according to their dependence on the system size M.

Comparison of the various M orders in (2.5) yields, first, the macroscopic law for $c_k(t)$ and, second, an equation for $\Pi(\xi, t)$. We start with the leading terms in (2.5), which are of order $M^{1/2}$. The macroscopic law is obtained if we require that the coefficients of $\partial\Pi/\partial\xi_k$ vanish for all $k = 1, 2,...$:

$$\dot{c}_k(t) = -\tfrac{1}{2}\sum_{i,j} K_{ij} c_i c_j (\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \tag{2.6}$$

Summation over the Kronecker delta shows that Eq. (2.6) is identical to Smoluchowski's equation (1.4). Thus, we have *derived* eq. (1.4), for general kernels K_{ij}, as the dominant term in the expansion of the master equation (1.1). As the initial condition for Eq. (2.6), or (1.4), we choose

$$c_k(0) = m_k(0)/M \qquad (k = 1, 2,...) \tag{2.7a}$$

This choice for $c_k(0)$ is convenient, since it implies that the fluctuations vanish at $t = 0$, i.e.,

$$\xi_k(0) = 0 \qquad (k = 1, 2,...) \tag{2.7b}$$

Equation (2.7b) is an immediate consequence of (1.6).

From the next order in (2.5), which are the terms of the order of unity, we find an equation for the probability distribution $\Pi(\xi, t)$:

$$\frac{\partial \Pi}{\partial t} = \tfrac{1}{2}\sum_{i,j} K_{ij}[D_{ij}(c_i\xi_j + c_j\xi_i) + \tfrac{1}{2}c_i c_j (D_{ij})^2]\,\Pi \tag{2.8}$$

The higher order terms in (2.5) are neglected. From the choice (2.7b) for $\xi_k(0)$ we infer that the initial condition for Eq. (2.8) is given by

$$\Pi(\xi, 0) = \delta(\xi) \tag{2.9}$$

Furthermore, we note that Eq. (2.8), with D_{ij} given by (2.3b), has the form of a multivariate linear Fokker–Planck equation,[2] with an *infinite* number of variables:

$$\frac{\partial \Pi}{\partial t} = -\sum_{k,j} A_{kj}(t)\frac{\partial}{\partial \xi_k}(\xi_j \Pi) + \frac{1}{2}\sum_{k,l} B_{kl}(t)\frac{\partial^2 \Pi}{\partial \xi_k\,\partial \xi_l} \tag{2.10}$$

and matrices $A_{kj}(t)$ and $B_{kl}(t)$ given by

$$A_{kj}(t) = -\sum_{i} K_{ij} c_i (\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \tag{2.11a}$$

$$B_{kl}(t) = \tfrac{1}{2}\sum_{i,j} K_{ij} c_i c_j (\delta_{ik} + \delta_{jk} - \delta_{i+j,k})(\delta_{il} + \delta_{jl} - \delta_{i+j,l}) \tag{2.11b}$$

This can be seen by inserting the explicit form (2.3b) of the operator D_{ij} into (2.8), and replacing the factor $(c_i\xi_j + c_j\xi_i)$ by $2c_i\xi_j$, which is allowed due to the symmetry with respect to i and j.

From the Fokker–Planck equation (2.10) one can readily derive equations for the average fluctuations $\langle \xi_m \rangle$ and the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$. The averages and covariances are defined, respectively, as

$$\langle \xi_m(t) \rangle \equiv \int d\boldsymbol{\xi}\, \xi_m \Pi(\boldsymbol{\xi}, t) \tag{2.12a}$$

and

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle = \langle \xi_m(t)\, \xi_n(t) \rangle - \langle \xi_m(t) \rangle \langle \xi_n(t) \rangle \tag{2.12b}$$

An equation for $\langle \xi_m(t) \rangle$ is obtained if we multiply Eq. (2.10) with ξ_m and integrate over all $\boldsymbol{\xi}$. The result shows that the averages $\langle \xi_m \rangle$ obey a set of *linear* differential equations as follows:

$$\frac{d}{dt} \langle \xi_m \rangle = \sum_j A_{mj}(t) \langle \xi_j \rangle \tag{2.13}$$

The initial condition for Eq. (2.13) is $\langle \xi_m(0) \rangle = 0$. This follows from (2.7b). As an immediate consequence, one finds that the average fluctuations vanish for all $t \geqslant 0$:

$$\langle \xi_m(t) \rangle = 0 \qquad (m = 1, 2, \ldots) \tag{2.14}$$

Hence, the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in (2.12b) are equal to $\langle \xi_m \xi_n \rangle$, and can be calculated by multiplying Eq. (2.10) with $\xi_m \xi_n$ and integrating over all $\boldsymbol{\xi}$. As a result, one finds the following set of linear, inhomogeneous differential equations:

$$\frac{d}{dt} \langle\langle \xi_m \xi_n \rangle\rangle = \sum_j \left(A_{nj} \langle\langle \xi_m \xi_j \rangle\rangle + A_{mj} \langle\langle \xi_n \xi_j \rangle\rangle \right) + B_{mn} \tag{2.15}$$

which are to be solved with the initial condition $\langle\langle \xi_m(0)\, \xi_n(0) \rangle\rangle = 0$. We remark that the solutions of Eq. (2.15) play an important role in this paper, for various reasons. One reason is that, as we shall see below, the probability distribution $\Pi(\boldsymbol{\xi}, t)$ in (2.10) is completely determined by $\langle\langle \xi_m \xi_n \rangle\rangle$.

A drastic simplification of Eq. (2.15) occurs if we transform from the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ to a new variable $e_{mn}(t)$, which is defined as

$$e_{mn}(t) \equiv \langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle - \delta_{mn} c_n(t) \tag{2.16}$$

In Ref. 1 it was found that this new variable is related in a simple way to the *factorial cumulants* $[m_k m_l]$ of the occupation numbers $\mathbf{m}$, since $[m_k m_l] \sim M e_{kl}$ as $M \to \infty$. In terms of $e_{mn}(t)$, Eq. (2.15) takes the following form:

$$\dot{e}_{mn}(t) = \sum_j (A_{nj} e_{mj} + A_{mj} e_{nj}) - K_{mn} c_m c_n \tag{2.17}$$

Equation (2.17) is also linear and inhomogeneous, but the inhomogeneity in (2.17) is much simpler than in (2.15). The initial condition for (2.17) is $e_{mn}(0) = -\delta_{mn} c_n(0)$.

Finally we discuss the implications of the conservation law (1.3) for the fluctuations ξ_k ($k = 1, 2, \ldots$). In combination with the conservation law (1.5) for the concentrations $c_k(t)$ and the definition (1.6) of ξ_k, Eq. (1.3) implies that

$$\sum_{k=1}^{\infty} k \xi_k = 0 \tag{2.18}$$

This relation between the fluctuations ξ_k can also be verified using the Fokker–Planck equation (2.10). The proof is elementary, and is omitted here. As a consequence of (2.18), we find the following relation between the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$, valid for all $m \geqslant 1$:

$$\sum_{n=1}^{\infty} n \langle\langle \xi_m \xi_n \rangle\rangle = 0 \tag{2.19a}$$

Similarly, a restriction on the factorial cumulants $e_{mn}(t)$ is found if we combine (2.19a) with (2.16). The result is

$$\sum_{n=1}^{\infty} n e_{mn}(t) = -m c_m(t) \tag{2.19b}$$

Conversely, it is also possible to derive (2.18) from (2.19a) or (2.19b). To see this, we multiply (2.19a) with m and sum over all m. The result shows that $\langle (\sum_m m \xi_m)^2 \rangle = 0$, which is possible only if (2.18) holds. Thus, Eqs. (2.18), (2.19a), and (2.19b) can be interpreted as different but equivalent representations of the conservation law for the total mass, expressed in terms of the fluctuations ξ.

3. $K_{ij} = i + j$: MONODISPERSE INITIAL CONDITIONS

In this section we study the fluctuations for the special case of a monodisperse initial distribution, corresponding to $m_k(0) = M\delta_{k1}$ or

$c_k(0) = \delta_{k1}$. For such initial conditions many properties of the fluctuations can be studied in detail. This section is subdivided into three parts, devoted, respectively, to (1) the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$, (2) the probability distribution $\Pi(\xi, t)$, and (3) the (two-time) correlation functions $\kappa_{nm}(t_2, t_1) \equiv \langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle$.

3.1. The Covariances

The covariances can be calculated from Eq. (2.15) or, equivalently, from (2.17) for the factorial cumulants $e_{mn}(t)$. For the model $K_{ij} = i + j$, Eq. (2.17) takes the form

$$\dot{e}_{mn} = \sum_{i+j=n} (i+j)\, c_i e_{mj} + \sum_{i+j=m} (i+j)\, c_i e_{nj} - n c_n \sum_j e_{mj} - m c_m \sum_j e_{nj} - (n+m)\, e_{mn} M_0 - 2 e_{mn} \tag{3.1}$$

where $M_0(t)$ is the zeroth moment of $c_k(t)$, which is given in (A.2) and (A.3). Since we assume that initially the system is monodisperse, Eq. (3.1) has to be solved subject to the initial condition

$$e_{mn}(0) = -\delta_{mn} c_n(0) = -\delta_{m1} \delta_{n1} \tag{3.2}$$

In Section 4 we solve (3.1) for *general* initial conditions. From this general result one finds that the solution for *monodisperse* initial conditions has a very simple form,

$$e_{mn}(t) = -e^{-2t} mn c_m(t)\, c_n(t) \tag{3.3}$$

where $c_k(t)$ is given in (A.11). It can readily be checked that $e_{mn}(t)$ in (3.3) satisfies both the initial condition (3.2) and the kinetic equation (3.1). In verifying (3.1) it is convenient to use Smoluchowski's equation (A.1) and the mass conservation law (1.5).

As an immediate consequence of (3.3) and the definition (2.16) of e_{mn}, one finds the following result for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$:

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle = \delta_{mn} c_n(t) - e^{-2t} mn c_m(t)\, c_n(t) \tag{3.4}$$

The relation (2.19a) between the covariances, which is a result of the conservation law for the total mass, can readily be verified with the use of Eq. (A.3) for the second moment, i.e., $M_2(t) = e^{2t}$. The *negativity* of $\langle\langle \xi_m \xi_n \rangle\rangle$ in (3.4) for $n \neq m$ is a reflection of the conservation law $\sum_k k \xi_k = 0$. The interpretation is simply that if, at some moment $t > 0$, the number of m-mers exceeds the average, i.e., if $\xi_m(t) > 0$, then most likely there will be fewer n-mers ($\xi_n < 0$).

3.2. The Probability Distribution

The result (3.4) for the covariances can be used to calculate the probability distribution $\Pi(\xi, t)$, which satisfies the linear Fokker–Planck equation (2.10), with the matrices A_{kj} and B_{kl} given by (2.11). From the literature[2,19] we recall that the solution of a linear Fokker–Planck equation has the form of a multivariate *Gaussian* distribution with zero average and covariance matrix $\langle\langle \xi_m \xi_n \rangle\rangle$. For the special case of the model $K_{ij} = i + j$ with monodisperse initial conditions, the probability distribution $\Pi(\xi, t)$ can be calculated explicitly.[20] The result is

$$\Pi(\xi, t) = (2\pi)^{1/2} e^t \delta\left(\sum_j j\xi_j\right) \prod_{j=1}^{\infty} g(\xi_j; c_j) \tag{3.5}$$

where $g(x; \sigma^2)$ is a one-dimensional Gaussian distribution with zero mean and variance σ^2, i.e.,

$$g(x; \sigma^2) = (2\pi\sigma^2)^{-1/2} \exp(-x^2/2\sigma^2) \tag{3.6}$$

In the direction $\xi^{(0)} = (1, 2, 3, \ldots)$, the Gaussian form has degenerated to a delta function as a result of the conservation law (2.18). The prefactor in (3.5) guarantees that $\Pi(\xi, t)$ is properly normalized. Comparison of (3.5) with Lushnikov's exact solution of the master equation[5] shows that both expressions have the same form: they consist of a product of independent Poisson distributions multiplied with a delta function representing the mass conservation law.

3.3. The Correlation Functions

The correlation functions $\kappa_{nm}(t_2, t_1)$ are defined as

$$\begin{aligned} \kappa_{nm}(t_2, t_1) &\equiv \langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle \\ &= \langle \xi_m(t_1)\, \xi_n(t_2) \rangle - \langle \xi_m(t_1) \rangle \langle \xi_n(t_2) \rangle \qquad (t_2 \geqslant t_1 \geqslant 0) \end{aligned} \tag{3.7}$$

As a result of (2.14), the second term on the right in (3.7) vanishes, so that in our case, $\kappa_{nm}(t_2, t_1)$ is also equal to $\langle \xi_m(t_1)\, \xi_n(t_2) \rangle$. The calculation of $\kappa_{nm}(t_2, t_1)$ consists of two steps. First, one calculates the conditional average $\overline{\xi_n(t_2)}$ of ξ_n at time t_2 for a given value $\xi(t_1)$ of the fluctuations at time t_1. The second step is to multiply $\overline{\xi_n(t_2)}$ with $\xi_m(t_1)$ and to average the result over all possible values of $\xi(t_1)$.

The calculation of the conditional averages $\overline{\xi_n(t_2)}$ for given initial fluctuations $\xi(t_1)$ proceeds as follows. From Eq. (2.13) it follows for the model

$K_{ij} = i + j$ that the averages $\overline{\xi_n(t)}$ satisfy the following set of differential equations:

$$\frac{d}{dt}\overline{\xi}_n = \sum_{i+j=n} (i+j)\, c_i \overline{\xi}_j - n c_n \sum_{j=1}^{\infty} \overline{\xi}_j - \overline{\xi}_n (1 + n M_0) \tag{3.8}$$

In the derivation of (3.8) we have used the conservation law (2.18). Equation (3.8) can be solved with the use of the generating function $\chi(x, t)$ of $\overline{\xi_n(t)}$, which is defined as

$$\chi(x, t) \equiv \sum_{n=1}^{\infty} \overline{\xi_n(t)} (e^{nx} - 1) \tag{3.9}$$

Multiplication of (3.8) with $(e^{nx} - 1)$ and summation over all n yields a partial differential equation for $\chi(x, t)$:

$$\frac{\partial \chi}{\partial t} = \chi \frac{\partial F}{\partial x} + F \frac{\partial \chi}{\partial x} - \chi \tag{3.10}$$

The generating function $F(x, t)$ of $c_k(t)$ has been defined in (A.4).

In order to solve Eq. (3.10), we transform from $\chi(x, t)$ to a new function $W(z, t)$:

$$W(z, t) \equiv \chi(x, t); \qquad z \equiv F(x, t) - x \tag{3.11}$$

and we find the following differential equation for $W(z, t)$:

$$\frac{\partial}{\partial t} [\log W(z, t)] = \frac{\partial F}{\partial x}(x, t) - 1 = [u'(z)\, e^{-t} - 1]^{-1} \tag{3.12}$$

In the derivation of (3.12) we have used Eq. (A.6) for $F(x, t)$ and the expression (A.8) for $\partial F/\partial x$ in terms of z and t. The solution of (3.12) is readily found to be

$$W(z, t) = W(z, t_1)[u'(z) - e^{t_1}]/[u'(z) - e^{t}] \tag{3.13}$$

This result makes it possible to express the generating function $\chi(x, t)$ in terms of its initial value $\chi(x, t_1)$. To see this, we introduce the point x_1, which is mapped at time t_1 onto the same value of z as (x, t), i.e.,

$$F(x_1, t_1) - x_1 \equiv z = F(x, t) - x \tag{3.14}$$

With this definition for x_1, one finds from (3.11) and (3.13) the following result for $\chi(x, t)$:

$$\begin{aligned} \chi(x, t) &= W(z, t_1)[u'(z) - e^{t_1}]/[u'(z) - e^{t}] \\ &= \chi(x_1, t_1)[u'(z) - e^{t_1}]/[u'(z) - e^{t}] \end{aligned} \tag{3.15}$$

An explicit expression for x_1 as a function of x, t, and t_1 can be obtained if we use Eq. (A.7) for $F(x, t)$:

$$\begin{aligned} x_1(x, t, t_1) &= x + F(x_1, t_1) - F(x, t) \\ &= x + (e^{t-t_1} - 1)\, F(x, t) \end{aligned} \tag{3.16}$$

Equation (3.15) with x_1 given by (3.16) represents the *exact solution* for the generating function $\chi(x, t)$ of the conditional averages $\overline{\xi_n(t)}$.

The relation (3.9) between $\chi(x, t)$ and $\overline{\xi_n(t)}$ can be inverted as follows. The averages $\overline{\xi_n(t)}$ are the coefficients of e^{nx} in the generating function $\chi(x, t)$. Hence, they can be written in the form of a contour integral in the complex plane:

$$\overline{\xi_n(t)} = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}}\, \chi(x, t) \tag{3.17}$$

where we have defined $y \equiv e^x$. The path of integration in (3.17) circles the origin in the complex y-plane once, and counterclockwise. Substitution into (3.17) of $\chi(x, t)$ in (3.15) and use of the definition (3.9) shows that $\overline{\xi_n(t)}$ depends linearly on the initial value $\xi(t_1)$:

$$\overline{\xi_n(t)} = \sum_{l=1}^{\infty} Y_{nl}(t, t_1)\, \xi_l(t_1) \tag{3.18}$$

where $Y_{nl}(t, t_1)$ is defined as

$$Y_{nl}(t, t_1) = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} (e^{lx_1} - 1) \frac{u'(z) - e^{t_1}}{u'(z) - e^t} \tag{3.19}$$

The matrix $Y_{nl}(t, t_1)$ is usually called the *evolution matrix* of the problem (3.8). The result (3.19) is valid for *general* initial conditions.

An explicit expression for $Y_{nl}(t, t_1)$ can be obtained for monodisperse initial conditions. For this purpose we transform from the variable $y = e^x$ in (3.19) to a new variable f, where f is the generating function (A.4) of $c_k(t)$. As a first step, we use the relation (A.8) between $u'(z)$ and $\partial f/\partial x$ to write $Y_{nl}(t, t_1)$ in the following form:

$$\begin{aligned} Y_{nl}(t, t_1) &= \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} (e^{lx_1} - 1) \left[e^{t_1 - t} + (1 - e^{t_1 - t}) \frac{\partial f}{\partial x}(x, t) \right] \\ &= -(1 - e^{t_1 - t})\, n c_n(t) + \frac{e^{t_1 - t}}{2\pi i} \oint \frac{dy}{y^{n+1}} e^{lx_1} \\ &\quad + \frac{1 - e^{t_1 - t}}{2\pi i} \oint \frac{df}{y^n} e^{lx_1} \end{aligned} \tag{3.20}$$

The variable y in (3.20) can be expressed in terms of f with the use of (A.9b). The result is

$$y = e^{t+\tau} f \exp(-\tau e^t f) \tag{3.21}$$

where we have introduced an auxiliary variable $\tau \equiv 1 - e^{-t}$. Similarly, the factor e^{x_1} in (3.20) can be expressed in terms of f with the use of (3.16):

$$\exp x_1 = y \exp\{(\tau - \tau_1)[(\exp t) f - 1]\} \tag{3.22}$$

We have defined $\tau_1 \equiv 1 - e^{-t_1}$. As a result of (3.21) and (3.22) one finds for the *first* integral on the right in (3.20)

$$\frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \exp(l x_1)$$

$$= l(\tau - \tau_1) \frac{(n\tau - l\tau_1)^{n-l-1}}{(n-l)!} \exp(l\tau_1 - n\tau) \tag{3.23a}$$

and similarly, for the *second* integral in (3.20),

$$\frac{1}{2\pi i} \oint \frac{df}{y^n} \exp(l x_1)$$

$$= (1 - \tau) \frac{(n\tau - l\tau_1)^{n-l-1}}{(n-l-1)!} \exp(l\tau_1 - n\tau) \tag{3.23b}$$

Substitution into (3.20) of the results (3.23a), (3.23b) finally gives the desired explicit expression for the evolution matrix $Y_{nl}(t, t_1)$:

$$Y_{nl}(t, t_1) = n \frac{\tau - \tau_1}{1 - \tau_1} \left[-c_n(t) + (1 - \tau) \frac{(n\tau - l\tau_1)^{n-l-1}}{(n-l)!} \exp(l\tau_1 - n\tau) \right] \tag{3.24}$$

Note that for $t \downarrow t_1$, the matrix Y_{nl} reduces to the identity matrix: $Y_{nl}(t_1, t_1) = \delta_{nl}$. This completes the first step in the calculation of $\kappa_{nm}(t_2, t_1)$.

The second step in the calculation of the correlation functions is to multiply (3.18) with $\xi_m(t_1)$ and to average over all possible values of $\xi(t_1)$. The result is

$$\kappa_{nm}(t_2, t_1) = \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1) \langle\langle \xi_l(t_1)\, \xi_m(t_1) \rangle\rangle$$

$$= Y_{nm}(t_2, t_1)\, c_m(t_1) - e^{-2t_1} m c_m(t_1) \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)\, l c_l(t_1) \tag{3.25}$$

In the derivation of (3.25) we used the result (3.4) for $\langle\langle \xi_l \xi_m \rangle\rangle$. The sum on the right-hand side of (3.25) can be calculated with the use of the integral representation (3.19) of Y_{nl}:

$$\sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)\, lc_l(t_1) = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \left[\frac{\partial F}{\partial x}(x_1, t_1) - 1 \right] \frac{u'(z) - e^{t_1}}{u'(z) - e^{t_2}}$$

$$= e^{t_1 - t_2} \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \left[\frac{\partial F}{\partial x}(x, t_2) - 1 \right]$$

$$= e^{t_1 - t_2} nc_n(t_2) \tag{3.26}$$

In the second step of (3.26) we used the relation (A.8) for $\partial F/\partial x$. In the third step we used the definition (A.4) of $F(x, t)$. Substitution of (3.26) into (3.25) gives the following expression for the correlation functions $\kappa_{nm}(t_2, t_1)$:

$$\kappa_{nm}(t_2, t_1) = Y_{nm}(t_2, t_1)\, c_m(t_1) - e^{-(t_1 + t_2)} mnc_m(t_1)\, c_n(t_2) \tag{3.27}$$

Clearly, Eq. (3.27) reduces to the previous result (3.4) if $t_2 \downarrow t_1$.

As an example, we consider the long-time behavior ($t_2 \to \infty$) of the autocorrelation functions $\kappa_{mm}(t_2, t_1)$. For large values of t_2, the second term on the right-hand side of (3.27) is of relative order e^{-t_2}, and can be neglected. The long-time behavior of the first term on the right in (3.27) can be determined from (3.24). Straightforward calculation shows that

$$\kappa_{mm}(t_2, t_1) \sim [-1 + m!\, e^{m\tau_1}/m^m(1 - \tau_1)]\, mc_m(t_1)\, c_m(t_2) \qquad (t_2 \to \infty) \tag{3.28}$$

From the explicit form (A.11) of $c_m(t_2)$ it follows that all autocorrelation functions $\kappa_{mm}(t_2, t_1)$ fall off exponentially as a function of t_2, so that (3.28) can be written in the form

$$\kappa_{mm}(t_2, t_1) \sim \sigma(m, t_1)\, e^{-t_2} \qquad (t_2 \to \infty) \tag{3.29}$$

The prefactor $\sigma(m, t_1)$ has a different sign for different combinations of m and t_1. This can be seen from (3.28). Analysis of the factor $[\cdots]$ in (3.28) shows that, for a fixed value of m, $\sigma(m, t_1)$ is *positive* if t_1 is sufficiently large ($t_1 > T_0$) and *negative* if t_1 is small ($t_1 < T_0$). The crossover time T_0 depends on the cluster size m, and for large m is given by $T_0(m) \sim \log m$.

4. $K_{ij} = i + j$: GENERAL INITIAL CONDITIONS

Next we study the fluctuations in the model $K_{ij} = i + j$ for *general* initial conditions. Our purpose is to gain insight into the *universal* properties of the fluctuations that apply for all initial distributions $m_k(0)$

($k = 1, 2, \ldots$). To this end, we calculate in Section 4.1 an *exact* expression for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in terms of their generating function. This result is used in the Sections 4.2 and 4.3 to calculate the asymptotic behavior of the covariances for *large cluster sizes* ($m, n \to \infty$), and in the *scaling limit.*

4.1. The Exact Solution

We start from Eq. (3.1) for the factorial cumulants $e_{mn}(t)$ with a general initial condition

$$e_{mn}(0) = -\delta_{mn} c_n(0) \tag{4.1}$$

Equation (3.1) can be solved with the use of generating functions. To show this, we introduce the generating function

$$h(x, y, t) \equiv \sum_{m,n} e_{mn}(t)\, e^{mx+ny} \tag{4.2a}$$

and, related to $h(x, y, t)$, a second function $H(x, y, t)$:

$$\begin{aligned} H(x, y, t) &\equiv \sum_{m,n} e_{mn}(t)(e^{mx} - 1)(e^{ny} - 1) \\ &= h(x, y, t) - h(x, 0, t) - h(0, y, t) + h(0, 0, t) \end{aligned} \tag{4.2b}$$

Our aim is to derive an equation for $H(x, y, t)$. For this purpose it is convenient to derive an equation for $h(x, y, t)$ first. Multiplication of Eq. (3.1) with e^{mx+ny} and summation over all m and n yields

$$\begin{aligned} &\frac{\partial h}{\partial t} - F(x, t)\frac{\partial h}{\partial x} - F(y, t)\frac{\partial h}{\partial y} \\ &\quad = \frac{\partial F}{\partial x}(x, t)[h - h(0, y, t)] \\ &\qquad + \frac{\partial F}{\partial y}(y, t)[h - h(x, 0, t)] - 2h \end{aligned} \tag{4.3}$$

where $F(x, t)$ is defined in (A.4). From (4.3) one can readily obtain equations for $h(x, 0, t)$, $h(0, y, t)$, and $h(0, 0, t)$ by putting $x = 0$, or $y = 0$, or $x = y = 0$. A suitable combination of these equations yields the following result for $H(x, y, t)$ in (4.2b):

$$\frac{\partial H}{\partial t} - F(x, t)\frac{\partial H}{\partial x} - F(y, t)\frac{\partial H}{\partial y} = \left[\frac{\partial F}{\partial x}(x, t) + \frac{\partial F}{\partial y}(y, t) - 2\right] H \tag{4.4a}$$

The initial condition for Eq. (4.4a) is

$$H(x, y, 0) = v(x) + v(y) - v(x + y) \tag{4.4b}$$

where we have defined $F(x, 0) \equiv v(x)$.

The differential equation (4.4) for $H(x, y, t)$ can be solved as follows. We transform the variables (x, y) to new variables (z_1, z_2):

$$z_1 \equiv F(x, t) - x; \qquad z_2 \equiv F(y, t) - y \tag{4.5a}$$

and we replace $H(x, y, t)$ by a new function $W(z_1, z_2, t)$, i.e.,

$$W(z_1, z_2, t) \equiv H(x, y, t) \tag{4.5b}$$

Substitution of (4.5) into (4.4a) and use of the differential equation (A.6) for $F(x, t)$ yields the following equation for $W(z_1, z_2, t)$:

$$\frac{\partial}{\partial t}[\log W(z_1, z_2, t)] = \frac{\partial F}{\partial x}(x, t) + \frac{\partial F}{\partial y}(y, t) - 2$$
$$= [u'(z_1)\, e^{-t} - 1]^{-1} + [u'(z_2)\, e^{-t} - 1]^{-1} \tag{4.6}$$

In the second step we used Eq. (A.8) for $\partial F/\partial x$. Integration of (4.6) is elementary. The result is

$$W(z_1, z_2, t) = W(z_1, z_2, 0) \frac{u'(z_1) - 1}{u'(z_1) - e^t} \frac{u'(z_2) - 1}{u'(z_2) - e^t} \tag{4.7}$$

As a consequence of (4.5b) we find for $H(x, y, t)$

$$H(x, y, t) = H(x_1, y_1, 0) \frac{u'(z_1) - 1}{u'(z_1) - e^t} \frac{u'(z_2) - 1}{u'(z_2) - e^t} \tag{4.8}$$

where $x_1 = x_1(x, t, 0)$ is defined by (3.14) or (3.16), and $y_1 = x_1(y, t, 0)$. Equation (4.8), in combination with the initial value $H(x, y, 0)$ in (4.4b), represents the *exact* solution for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in terms of their generating function.

We add two remarks. The first is that, for monodisperse initial conditions, Eq. (4.8) can be inverted to yield Eq. (3.3) for $e_{mn}(t)$. This can be seen from (4.4b), where for monodisperse initial conditions $v(x) = e^x - 1$. Hence

$$H(x_1, y_1, 0) = -(e^{x_1} - 1)(e^{y_1} - 1) \tag{4.9a}$$

Furthermore, it follows from (A.8) for $\partial F/\partial x$ that

$$u'(z_1)-1=\left[\frac{\partial F}{\partial x}(x_1,0)-1\right]^{-1}=(e^{x_1}-1)^{-1} \tag{4.9b}$$

Combination of (4.8) with (4.9a), (4.9b), and (A.8) gives

$$H(x,y,t)=-e^{-2t}\left[\frac{\partial F}{\partial x}(x,t)-1\right]\left[\frac{\partial F}{\partial y}(y,t)-1\right] \tag{4.10}$$

and inversion of (4.10) immediately yields (3.3) for $e_{mn}(t)$. The second remark is that, for our purposes, Eq. (4.8) is not the most convenient form for $H(x, y, t)$. An alternative representation that will be used below can be obtained from (4.8) if we use Eq. (A.8) for $\partial F/\partial x$:

$$H(x,y,t)=H(x_1,y_1,0)\left[e^{-t}+\tau\frac{\partial F}{\partial x}(x,t)\right]\left[e^{-t}+\tau\frac{\partial F}{\partial y}(y,t)\right] \tag{4.11}$$

The value of τ is again given by $\tau=1-e^{-t}$.

4.2. Fluctuations at Large Cluster Sizes ($m, n\to\infty$)

In order to calculate the asymptotic behavior of $e_{mn}(t)$ at large cluster sizes, we consider first an *exact* expression for $e_{mn}(t)$ in the form of a double contour integral in the complex plane:

$$e_{mn}(t)=\left(\frac{1}{2\pi i}\right)^2\oint\frac{dw_1}{w_1^{m+1}}\oint\frac{dw_2}{w_2^{n+1}}H(x,y,t) \tag{4.12}$$

where $w_1\equiv e^x$ and $w_2\equiv e^y$. The integration paths in (4.12) circle the origin in the w_1 and w_2 planes once in the counterclockwise direction.

The asymptotic behavior of e_{mn} for large values of m and n can be obtained from (4.12) with the use of the saddlepoint method. From (A.7) and (A.12) we know that the function $x(F, t)$, or, equivalently, $w_1(F, t)$, has a saddle point at $F_s(t)=e^{-t}u(z_s)$, where the value of $z_s(t)$ is determined by (A.12). The corresponding values of $x(F, t)$ and $w_1(F, t)$ at the saddle point are $x_s(t)=e^{-t}u(z_s)-z_s$ and $w_s(t)=e^{x_s(t)}$. Obviously, $y(F, t)$ and $w_2(F, t)$ also have a saddle point at $F=F_s(t)$.

The saddlepoint method works as follows. We calculate the w_1 integral in (4.12) along the contour $w_1=w_s(t)\,e^{i\varphi_1}$, with $-\pi<\varphi_1\leqslant\pi$. Similarly, the w_2 integral is calculated along the circle $w_2=w_s(t)\,e^{i\varphi_2}$, with $-\pi<\varphi_2\leqslant\pi$. With this choice for the contours in (4.12), the integrand $H(x, y, t)$ is sharply peaked about the point $(x, y)=(x_s(t), x_s(t))$ if m and n are large.

Consequently, one finds from (4.12), with $H(x, y, t)$ given by (4.11), that for large cluster sizes

$$\begin{aligned} e_{mn}(t) &\sim H(x_1^s, x_1^s, 0)\left(\frac{\tau}{2\pi i}\right)^2 \\ &\quad \times \oint \frac{dw_1}{w_1^{m+1}} \oint \frac{dw_2}{w_2^{n+1}} \frac{\partial F}{\partial x}(x, t) \frac{\partial F}{\partial y}(y, t) \\ &\sim \tau^2 H(x_1^s, x_1^s, 0)\, mnc_m(t)\, c_n(t) \qquad (m, n \to \infty) \end{aligned} \tag{4.13}$$

where $x_1^s(t) \equiv x_1(x_s, t, 0)$. In the second step of (4.13) we used the definition (A.4) of $F(x, t)$. The asymptotic behavior of the concentrations $c_k(t)$ as $k \to \infty$ is given in (A.14).

4.3. The Scaling Limit

Next we show that the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ approach a *scale-invariant* form, *independent of the initial conditions*, in the scaling limit. The scaling limit is the limit where the average cluster size diverges: $s(t) \to \infty$ and $m, n \to \infty$ with $m/s(t)$ and $n/s(t)$ fixed. As a definition of the "average cluster size" we choose

$$s(t) \equiv M_2(t)/M_1(t) = M_2(0)\, e^{2t} \tag{4.14}$$

but different choices for $s(t)$ lead to qualitatively the same results. The scaling behavior of the macroscopic solution $c_k(t)$ is summarized in Appendix A.

We start again from $H(x, y, t)$ in the form (4.11). Before considering $\langle\langle \xi_m \xi_n \rangle\rangle$ itself, we show first that the generating function $H(x, y, t)$ approaches a scale-invariant form, independent of the initial conditions. From Appendix A we know that the generating function $(\partial F/\partial x)(x, t)$ in (4.11), and hence also $(\partial F/\partial y)(y, t)$, approaches a scaling form in the scaling limit (S) as follows:

$$\begin{aligned} &\frac{\partial F}{\partial x}(x, t) \xrightarrow{\text{S}} \psi(\rho_1); \qquad \rho_1 \equiv -xs(t) \\ &\frac{\partial F}{\partial y}(y, t) \xrightarrow{\text{S}} \psi(\rho_2); \qquad \rho_2 \equiv -ys(t) \end{aligned} \tag{4.15}$$

where $\psi(\rho)$ is defined in (A.16), i.e., $\psi(\rho) = (1 + 2\rho)^{-1/2}$. Furthermore, the scaling behavior of x_1 and y_1 in (4.11) follows from (3.16) and (A.15) as

$$\begin{aligned} x_1 &\xrightarrow{\text{S}} -[M_2(0)\, s(t)]^{-1/2}[(1 + 2\rho_1)^{1/2} - 1] \\ y_1 &\xrightarrow{\text{S}} -[M_2(0)\, s(t)]^{-1/2}[(1 + 2\rho_2)^{1/2} - 1] \end{aligned} \tag{4.16}$$

Thus, in the scaling limit, x_1 vanishes proportional to $s(t)^{-1/2}$, albeit non-uniformly in the scaling variable $\rho_1 = -xs(t)$. Similarly, y_1 vanishes non-uniformly in ρ_2. It follows that the factor $H(x_1, y_1, 0)$ in (4.11) vanishes as $s(t) \to \infty$, since we know from (4.4b) that $H(0, 0, 0) = 0$. Expansion of $H(x_1, y_1, 0)$ about $x_1 = y_1 = 0$ gives

$$H(x_1, y_1, 0) \xrightarrow{\text{S}} -v''(0)\, x_1\, y_1 = -M_2(0)\, x_1\, y_1 \tag{4.17}$$

The scaling behavior of $H(x, y, t)$ is obtained if we substitute the results (4.15)–(4.17) into Eq. (4.11):

$$H(x, y, t) \xrightarrow{\text{S}} -s(t)^{-1}[1-\psi(\rho_1)][1-\psi(\rho_2)] \tag{4.18}$$

Clearly this result for $H(x, y, t)$ is independent of the initial conditions.

As an immediate consequence of (4.18) one finds that $e_{mn}(t)$ also approaches a scale-invariant form as $s(t) \to \infty$. This can be seen by substituting (4.18) into (4.12). The result is

$$e_{mn}(t) \xrightarrow{\text{S}} -s(t)^{-1} \left(\frac{1}{2\pi i}\right)^2 \oint \frac{dw_1}{w_1^{m+1}} \oint \frac{dw_2}{w_2^{n+1}} [1-\psi(\rho_1)][1-\psi(\rho_2)]$$

$$\xrightarrow{\text{S}} -s(t)^{-1}\, mnc_m(t)\, c_n(t) \tag{4.19}$$

In the second step of (4.19) we used Eq. (4.15) for $\partial F/\partial x$ and $\partial F/\partial y$. An alternative representation of $e_{mn}(t)$ can be obtained from the scaling behavior (A.17) of $c_k(t)$. One finds that, in the scaling limit, $e_{mn}(t)$ can be described by a *scaling function* $\Phi(r_1, r_2)$ as follows:

$$e_{mn}(t) \xrightarrow{\text{S}} s(t)^{-3}\, \Phi(r_1, r_2) \tag{4.20a}$$

where $r_1 \equiv m/s(t)$, $r_2 \equiv n/s(t)$, and $\Phi(r_1, r_2)$ is defined as

$$\Phi(r_1, r_2) \equiv -r_1 r_2 \varphi(r_1)\, \varphi(r_2) \tag{4.20b}$$

The explicit form of $\varphi(r)$ is given in (A.17b).

The scaling behavior of the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ follows from (4.20) and (2.16) if, in addition, we replace the Kronecker delta in (2.16) by $s(t)^{-1}\, \delta(r_1 - r_2)$. The result is

$$\langle\langle \xi_m \xi_n \rangle\rangle \xrightarrow{\text{S}} s(t)^{-3}\, \Psi(r_1, r_2) \tag{4.21a}$$

where $\Psi(r_1, r_2)$ is related to $\Phi(r_1, r_2)$ by

$$\Psi(r_1, r_2) = \delta(r_1 - r_2)\, \varphi(r_1) + \Phi(r_1, r_2) \tag{4.21b}$$

Equations (4.20) and (4.21) represent the main result of this section. They show very clearly that, at least for the model $K_{ij}=i+j$, the factorial cumulants $e_{mn}(t)$ and the cumulants $\langle\langle \xi_m \xi_n \rangle\rangle$ approach a simple, scale-invariant form in the scaling limit that does not depend on the details of the initial distribution.

5. $K_{ij}=1$: MONODISPERSE INITIAL CONDITIONS

Next we discuss the second exactly solvable example of this paper, which is the model $K_{ij}=1$. In this section we restrict ourselves to monodisperse initial conditions, $m_k(0)=M\delta_{k1}$, and we consider, respectively, the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ (Section 5.1), the probability distribution $\Pi(\xi, t)$ (Section 5.2), and the correlation functions $\langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle$ (Section 3). Some results concerning the macroscopic law for this model are summarized in Appendix A.

5.1. The Covariances

We start again from Eq. (2.17) for the factorial cumulants $e_{mn}(t)$. In the case of the model $K_{ij}=1$, Eq. (2.17) reads

$$\dot{e}_{mn} = \sum_{i+j=m} c_i e_{nj} + \sum_{i+j=n} c_i e_{mj} - c_n \sum_j e_{mj} - c_m \sum_j e_{nj} - 2M_0 e_{mn} - c_m c_n \tag{5.1}$$

where $M_0(t)$ is the zeroth moment of $c_k(t)$, which is given below Eq. (A.23). The initial condition for Eq. (5.1) is $e_{mn}(0)=-\delta_{m1}\delta_{n1}$. The solution of (5.1) corresponding to this initial condition has the form

$$e_{mn}(t)=[A(t)+B(t)(m+n)+C(t)\, mn]\, c_m(t)\, c_n(t) \tag{5.2}$$

where $A(t)$, $B(t)$, and $C(t)$ are given by

$$A(t)=-\tfrac{1}{3}t(4+t)(1+t)/(2+t)^2 \tag{5.3a}$$

$$B(t)=\tfrac{1}{3}t(4+t)/(2+t)^2 \tag{5.3b}$$

$$C(t)=-\tfrac{4}{3}(3+t)/(2+t)^2 \tag{5.3c}$$

It can readily be verified that $e_{mn}(t)$ in (5.2) and (5.3) satisfies Eq. (5.1). In these calculations it is convenient to use the explicit form (A.23) of $c_k(t)$. Furthermore, we note that the solution given in (5.2) and (5.3) satisfies the initial condition, since $e_{mn}(0)=C(0)\,\delta_{m1}\delta_{n1}$, with $C(0)=-1$. As a remark,

we add that it is also possible to solve Eq. (5.1) constructively. This will be done in Section 6 for general initial conditions. From these results one finds (5.2) and (5.3) as a special case if the initial distribution is monodisperse.

As an immediate consequence of the definition (2.16) of $e_{mn}(t)$, one finds the following result for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$:

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle = \delta_{mn} c_n(t) + [A(t) + B(t)(m+n) + C(t)\, mn]\, c_m(t)\, c_n(t) \qquad (5.4)$$

The property (2.19a), which is a consequence of the conservation law $\sum_n n\xi_n = 0$, can readily be verified from (5.4) if one uses Eq. (A.22) for the second moment $M_2(t)$, i.e., $M_2(t) = 1 + t$, and the explicit form (5.3) of $A(t)$, $B(t)$, and $C(t)$.

The result (5.2) or (5.4) for the covariances in the model $K_{ij} = 1$ differs notably from the corresponding result (3.3) for the model $K_{ij} = i + j$. Apart from a term proportional to $mnc_m c_n$, Eq. (5.2) contains additional terms, with coefficients $A(t)$ and $B(t)$. The relative importance of these terms is different in different limits. For large cluster sizes ($m, n \to \infty$) the terms proportional to $A(t)$ and $B(t)$ are negligible, and only the third term in (5.2) contributes. However, at large times ($t \to \infty$) the first term in (5.2), corresponding to $A(t)$, dominates, and all three terms are important in the scaling limit, as we shall see in Section 6.

Another striking difference between the present result (5.2) and Eq. (3.3) for the model $K_{ij} = i + j$ is the *sign* of $e_{mn}(t)$. In (3.3) the sign is manifestly negative, whereas for $K_{ij} = 1$, the result is more complicated. If the cluster sizes m and n are comparable, i.e., if $m/n \simeq 1$, then $e_{mn}(t)$ in (5.2) is strictly negative for all $t > 0$. However, for a fixed value of m, with $n \to \infty$, it follows from (5.2) and (5.3) that

$$e_{mn}(t) \sim \frac{t^2 - 4(m-1)\, t - 12m}{3(2+t)^2} nc_m(t)\, c_n(t) \qquad (n \to \infty) \qquad (5.5)$$

Clearly, $e_{mn}(t)$ is *negative* for short times and *positive* for sufficiently large values of t. This implies that, for sufficiently large times, an excess of (small) m-mers is positively correlated with an excess of large n-mers. The explanation for this phenomenon will be given below.

5.2. The Probability Distribution

The probability distribution $\Pi(\xi, t)$ for the model $K_{ij} = 1$ with a monodisperse initial condition again has a multivariate Gaussian form, with zero average and covariance matrix $\langle\langle \xi_m \xi_n \rangle\rangle$, where $\langle\langle \xi_m \xi_n \rangle\rangle$ is given

by (5.4). As in Section 3.2, it is possible to derive an explicit expression for $\Pi(\xi, t)$.[20] The result is

$$\Pi(\xi, t) = 2\pi[B(t)]^{-1/2}\,\delta\left(\sum_j j\xi_j\right) g\left(\sum_j \xi_j; v_0\right) \prod_{j=1}^{\infty} g(\xi_j; c_j) \qquad (5.6a)$$

where $g(x; \sigma^2)$ is the one-dimensional Gaussian distribution (3.6). Furthermore, the value of $B(t)$ is given in (5.3b), and $v_0(t)$ is defined as

$$v_0(t) = 2(12 + 6t + t^2)/[t(4 + t)(2 + t)] \qquad (5.6b)$$

We note that the form of $\Pi(\xi, t)$ in (5.6) is *different* from the corresponding result (3.5) for the model $K_{ij} = i + j$. Equation (5.6a) contains, apart from a delta function, representing the mass conservation law $\sum_k k\xi_k = 0$, and an infinite product of independent Gaussian distributions $g(\xi_k; c_k)$, an *extra factor*, namely $g(\sum_j \xi_j; v_0)$. The extra factor imposes an additional restriction on the fluctuations $\sum_j \xi_j$ in the total number of clusters $\sum_j m_j$. This restriction is very weak at short times, since $v_0(t) \to \infty$ as $t \downarrow 0$ and becomes more serious at large times, where $v_0(t) \sim M_0(t) \sim 2/t$. Thus, at short times, only the effects of the mass conservation law are noticeable, and $e_{mn}(t)$ in (5.2) is *negative* for all m and n. At larger times there is an additional tendency to reduce the fluctuations in the total number of clusters. Consequently, an excess of (small) m-mers implies that, most likely, several smaller clusters have combined to form a few large n-mers, so as to reduce the fluctuation in the total number of clusters. This explains why $e_{mn}(t)$ in (5.5), with $n \gg m$, becomes *positive* for sufficiently large values of t.

5.3. The correlation Functions

In order to calculate the correlation functions $\kappa_{nm}(t_2, t_1)$ with $t_2 \geqslant t_1$ we consider first the conditional averages $\overline{\xi_n(t)}$ for given initial fluctuations $\xi(t_1)$. The time evolution of these averages $\overline{\xi_n(t)}$ is described by Eq. (2.13), which for the model $K_{ij} = 1$ takes the form

$$\frac{d}{dt}\overline{\xi}_n = \sum_{i+j=n} c_i \overline{\xi}_j - c_n \sum_j \overline{\xi}_j - \overline{\xi}_n M_0 \qquad (5.7)$$

In order to solve Eq. (5.7), we introduce again the generating function $\chi(x, t)$ of $\overline{\xi}_n$, which is defined in (3.9). Multiplication of both sides of (5.7) with $(e^{nx} - 1)$ and summation over all n yields a closed equation for $\chi(x, t)$,

$$\frac{\partial \chi}{\partial t}(x, t) = F(x, t)\,\chi(x, t) \qquad (5.8)$$

where $F(x, t)$ is the generating function (A.4) of $c_k(t)$. Integration of Eq. (5.8) is elementary. The result is

$$\chi(x, t) = \chi(x, t_1) \exp\left[\int_{t_1}^{t} d\tau\, F(x, \tau)\right] = \chi(x, t_1)\, T(x, t_1, t) \tag{5.9a}$$

where we have introduced the notation

$$T(x, t_1, t) = [1 - t_1 v(x)/2]^2/[1 - tv(x)/2]^2 \tag{5.9b}$$

with $v(x) \equiv F(x, 0)$. In the second step of (5.9a) we have used the explicit form (A.20) of the generating function $F(x, t)$. Equation (5.11) relates the fluctuations at time t to the initial fluctuations at time t_1.

An explicit expression for the averages $\overline{\xi_n(t)}$ in terms of their initial values $\xi(t_1)$ can be obtained if we substitute the generating function result (5.9) into Eq. (3.17). One finds that $\overline{\xi_n(t)}$ and $\xi(t_1)$ are related through an evolution matrix $Y(t, t_1)$:

$$\overline{\xi_n(t)} = \sum_{l=1}^{\infty} Y_{nl}(t, t_1)\, \xi_l(t_1) \tag{5.10a}$$

where $Y_{nl}(t, t_1)$ is given by

$$Y_{nl}(t, t_1) = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} (y^l - 1)\, T(x, t_1, t) \tag{5.10b}$$

with $y \equiv e^x$. In order to calculate $Y_{nl}(t, t_1)$, it is convenient to write (5.10b) in the form

$$Y_{nl}(t, t_1) = Q_{n-l}(t, t_1) - Q_n(t, t_1) \tag{5.11a}$$

where $Q_k(t, t_1)$ is defined as

$$Q_k(t, t_1) \equiv \frac{1}{2\pi i} \oint \frac{dy}{y^{k+1}}\, T(x, t_1, t) \tag{5.11b}$$

For monodisperse initial conditions, where $v(x) = e^x - 1$, one can express $T(x, t_1, t)$ in (5.9b) in terms of the function $\partial F/\partial x$ in (A.21) as follows:

$$\begin{aligned} T(x, t_1, t) &= \left(1 + \frac{t_1}{2} - \frac{t_1}{2} e^x\right)^2 e^{-x} \frac{\partial F}{\partial x}(x, t) \\ &= \left(1 + \frac{t_1}{2} - \frac{t_1}{2} e^x\right)^2 e^{-x} \sum_{l=1}^{\infty} l c_l(t)\, e^{lx} \end{aligned} \tag{5.12}$$

According to (5.11b), $Q_k(t, t_1)$ is the coefficient of e^{kx} in $T(x, t, t_1)$. With the use of (5.12) this coefficient is readily found as

$$Q_k(t, t_1) = (1 + \tfrac{1}{2}t_1)^2(k+1)\, c_{k+1}(t) - t_1(1 + \tfrac{1}{2}t_1)\, kc_k(t) + (\tfrac{1}{2}t_1)^2(k-1)\, c_{k-1}(t) \tag{5.13}$$

The evolution matrix $Y_{nl}(t, t_1)$ is now determined by (5.11a) in combination with (5.13).

The next step in the calculation of the correlation functions $\kappa_{nm}(t_2, t_1)$ is to multiply (5.10a) with $\xi_m(t_1)$ and to average over all possible values of $\xi(t_1)$:

$$\kappa_{nm}(t_2, t_1) = \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1) \langle\!\langle \xi_l(t_1)\, \xi_m(t_1) \rangle\!\rangle = [Y_{nm}(t_2, t_1) + S_{nm}(t_2, t_1)]\, c_m(t_1) \tag{5.14a}$$

In the second step of (5.14a) we used Eq. (5.4) for the covariances $\langle\!\langle \xi_l(t_1)\, \xi_m(t_1) \rangle\!\rangle$, and we introduced the notation $S_{nm}(t_2, t_1)$ for the sum

$$S_{nm}(t_2, t_1) \equiv \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)[A(t_1) + B(t_1)(m+l) + C(t_1)\, ml]\, c_l(t_1) \tag{5.14b}$$

A different representation of S_{nm} is obtained if we insert into (5.14b) the definition (5.10b) of Y_{nl}. The result is

$$S_{nm}(t_2, t_1) = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}}\, I(x, t_1)\, T(x, t_1, t_2) \tag{5.15a}$$

with $I(x, t_1)$ given by

$$\begin{aligned} I(x, t_1) &= \sum_{l=1}^{\infty} [A(t_1) + B(t_1)(m+l) + C(t_1)\, ml]\, c_l(t_1)(e^{lx} - 1) \\ &= [A(t_1) + B(t_1)\, m]\, F(x, t_1) \\ &\quad + [B(t_1) + C(t_1)\, m]\left[\frac{\partial F}{\partial x}(x, t_1) - 1\right] \end{aligned} \tag{5.15b}$$

Equation (5.15) is a convenient starting point for the calculation of $S_{nm}(t_2, t_1)$.

We consider the various terms in $I(x, t_1)$ separately. The first term on the right in (5.15b), proportional to $F(x, t_1)$, gives a contribution to S_{nm} of the form $[A(t_1) + B(t_1)\, m]\, R_n(t_2, t_1)$, with $R_n(t_2, t_1)$ defined as

$$R_n(t_2, t_1) \equiv \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}}\, F(x, t_1)\, T(x, t_1, t_2) \tag{5.16}$$

With the use of Eqs. (A.20) and (A.21), in combination with the definition (5.9b) of $T(x, t_1, t_2)$, $R_n(t_2, t_1)$ can be calculated as follows:

$$\begin{aligned} R_n(t_2, t_1) &= \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} v(x) \left[1 - \frac{t_1}{2} v(x) \right] e^{-x} \frac{\partial F}{\partial x}(x, t_2) \\ &= -\left(1 + \frac{t_1}{2} \right) (n+1)\, c_{n+1}(t_2) \\ &\quad + (1 + t_1)\, n c_n(t_2) - \frac{t_1}{2} (n-1)\, c_{n-1}(t_2) \\ &= -\frac{1}{2} \left[\frac{(2+t_1)(t_2 - 2n)}{2 + t_2} + \frac{t_1(2n - 2 - t_2)}{t_2} \right] c_n(t_2) \end{aligned} \tag{5.17}$$

In the second and third steps of (5.17) we used, respectively, the definition (A.4) of $F(x, t)$ and the explicit form (A.23) of $c_k(t)$. Furthermore, the terms in $I(x, t_1)$ proportional to $\partial F/\partial x$ lead to an integral of the form

$$\begin{aligned} &\frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \frac{\partial F}{\partial x}(x, t_1)\, T(x, t_1, t_2) \\ &\quad = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \frac{\partial F}{\partial x}(x, t_2) \\ &\quad = n c_n(t_2) \end{aligned} \tag{5.18}$$

Finally, the remaining terms in (5.15b), i.e., $[B(t_1) + C(t_1)\, m]$, yield an integral of the form (5.11b) with $k = n$. Combination of (5.15)–(5.18) gives an explicit expression for $S_{nm}(t_2, t_1)$ in (5.14b). The result is

$$\begin{aligned} S_{nm}(t_2, t_1) &= [A(t_1) + B(t_1)\, m]\, R_n(t_2, t_1) \\ &\quad + [B(t_1) + C(t_1)\, m][n c_n(t_2) - Q_n(t_2, t_1)] \end{aligned} \tag{5.19}$$

where $R_n(t_2, t_1)$ and $Q_n(t_2, t_1)$ are given in (5.17) and (5.13), respectively. In combination with Eq. (5.14a) this gives an explicit expression for the two-time correlation functions $\kappa_{nm}(t_2, t_1)$ in the model $K_{ij} = 1$.

It can readily be verified that Eq. (5.14a) for the correlation functions $\kappa_{nm}(t_2, t_1)$ reduces to the previous result (5.4) for $\ll \xi_m(t_1)\, \xi_n(t_1) \gg$ in the limit $t_2 \downarrow t_1$. To see this, we note that Eq. (5.13), in combination with Eq. (A.23) for $c_k(t)$, implies that $Q_k(t_1, t_1) = \delta_{k0}$. As a result, $Y_{nm}(t_2, t_1)$ in (5.11) reduces to the identity matrix as $t_2 \downarrow t_1$, i.e.,

$$Y_{nm}(t_1, t_1) = \delta_{nm} \tag{5.20a}$$

Furthermore, the definition (5.16) of R_n shows that $R_n(t_1, t_1) = c_n(t_1)$. As a consequence, one finds from Eq. (5.19) that

$$S_{nm}(t_1, t_1) = [A(t_1) + B(t_1)(m+n) + C(t_1)\, mn]\, c_n(t_1) \qquad (5.20b)$$

Substitution of (5.20a), (5.20b) into (5.14a) immediately yields Eq. (5.4) for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$, as it should.

To obtain insight into the time dependence of the correlation functions $\kappa_{nm}(t_2, t_1)$ in (5.14a), we consider the special case $m = n$, and we restrict ourselves to large times ($t_2 \to \infty$). The diagonal elements of the evolution matrix $Y_{nm}(t_2, t_1)$ with $t_2 \to \infty$ can be calculated from (5.11a) and (5.13). One finds that

$$Y_{mm}(t_2, t_1) \sim [-m + (t_1/2)^2]\, c_m(t_2) \qquad (t_2 \to \infty) \qquad (5.21a)$$

Furthermore, the matrix elements $S_{mm}(t_2, t_1)$ can be determined from (5.19) with the use of (5.17) for $R_m(t_2, t_1)$ and (5.13) for $Q_m(t_2, t_1)$. Straightforward calculation yields the following remarkably simple result:

$$S_{mm}(t_2, t_1) \sim m c_m(t_2) \qquad (t_2 \to \infty) \qquad (5.21b)$$

Combination of (5.21a), (5.21b) with (5.14a) finally gives a very simple expression for the autocorrelation functions $\kappa_{mm}(t_2, t_1)$ as $t_2 \to \infty$:

$$\begin{aligned} \kappa_{mm}(t_2, t_1) &\sim (t_1/2)^2\, c_m(t_1)\, c_m(t_2) \\ &\sim (t_1/t_2)^2\, c_m(t_1) \qquad (t_2 \to \infty) \end{aligned} \qquad (5.22)$$

In the second step of (5.22) we used the explicit form of $c_m(t_2)$, i.e., Eq. (A.23). The result (5.22) for the autocorrelation functions in the model $K_{ij} = 1$ differs markedly from the corresponding result (3.28) or (3.29) for $K_{ij} = i + j$. First, for $K_{ij} = 1$ the autocorrelation functions fall off *algebraically*, rather than exponentially, as a function of t_2. Second, the sign of $\kappa_{mm}(t_2, t_1)$ in (5.22) is *positive* for all possible values of m and t_1. Thus, the crossover effect discussed below Eq. (3.29) does not occur in the model $K_{ij} = 1$.

6. $K_{ij} = 1$: GENERAL INITIAL CONDITIONS

In this section we study the universal properties of the fluctuations in the model $K_{ij} = 1$ that apply for all initial distributions $m_k(0)$ ($k = 1, 2, \ldots$). The organization of this section is the same as that of Section 4. First (in Section 6.1) we derive an exact expression for the factorial cumulants $e_{mn}(t)$ in terms of their generating function. This result is used in Sections 6.2 and 6.3, respectively, to calculate the asymptotic behavior $e_{mn}(t)$ for large cluster sizes ($m, n \to \infty$) and in the scaling limit.

6.1. The Exact Solution

We start from (5.1) for $e_{mn}(t)$, with the general initial condition (4.1), and we introduce again the generating functions $h(x, y, t)$ and $H(x, y, t)$, which were defined in (4.2). Along the same lines as in (4.3) and (4.4) we find from (5.1) an equation for $H(x, y, t)$,

$$\frac{\partial H}{\partial t} = [F(x, t) + F(y, t)]\, H - F(x, t)\, F(y, t) \tag{6.1}$$

where $F(x, t)$ is the generating function (A.4) of $c_k(t)$. The solution method for (6.1) is standard. With the use of Eq. (A.20) for $F(x, t)$, one finds the following result for $H(x, y, t)$:

$$H(x, y, t) = \{[1 - \tfrac{1}{2}tv(x)][1 - \tfrac{1}{2}tv(y)]\}^{-2}\, V(x, y, t) \tag{6.2a}$$

where $V(x, y, t)$ is defined as

$$V(x, y, t) \equiv H(x, y, 0) - v(x)\, v(y)\, t \times \{1 - \tfrac{1}{4}t[v(x) + v(y)] + \tfrac{1}{12}t^2 v(x)\, v(y)\} \tag{6.2b}$$

and $H(x, y, 0)$ is given in (4.4b). The factorial cumulants $e_{mn}(t)$ can in principle be determined from the integral representation (4.12).

For the special case of monodisperse initial conditions, Eq. (6.2) can be inverted to yield the previous result (5.2), (5.3) for $e_{mn}(t)$. The simplest way to see this is to start from Eqs. (5.2) and (5.3) and to calculate the corresponding generating function $H(x, y, t)$. As the result, one finds (6.2), with $v(x) = e^x - 1$. The calculations are straightforward, and can be omitted here.

6.2. Fluctuations at Large Cluster Sizes ($m, n \to \infty$)

The asymptotic behavior of $e_{mn}(t)$ at large cluster sizes can be calculated from Eq. (4.12), with $H(x, y, t)$ given by (6.2). For this purpose it is convenient to rewrite $H(x, y, t)$ with the use of Eq. (A.21) for the generating function $(\partial F/\partial x)(x, t)$ as follows:

$$H(x, y, t) = a(x, y, t) \frac{\partial F}{\partial x}(x, t) \frac{\partial F}{\partial y}(y, t) \tag{6.3a}$$

where $a(x, y, t)$ is defined as

$$a(x, y, t) = [v'(x)\, v'(y)]^{-1}\, V(x, y, t) \tag{6.3b}$$

The dominant contribution to the integral (4.12) for *large* values of m and n comes from the poles in $H(x, y, t)$ at the point $(x, y) = (x_0(t), x_0(t))$, where $x_0(t)$ is implicitly defined by $v(x_0) = 2/t$. Therefore the leading behavior of $e_{mn}(t)$ is obtained if we replace the function $a(x, y, t)$ in (6.3a) with its value *at* the pole. Thus we find from (4.12) that for large values of m and n

$$e_{mn}(t) \sim a(x_0, x_0, t) \left(\frac{1}{2\pi i}\right)^2 \times \oint \frac{dw_1}{w_1^{m+1}} \oint \frac{dw_2}{w_2^{n+1}} \frac{\partial F}{\partial x}(x, t) \frac{\partial F}{\partial y}(y, t) \sim a(x_0, x_0, t)\, mnc_m(t)\, c_n(t) \qquad (m, n \to \infty) \tag{6.4a}$$

The asymptotic behavior of the concentrations $c_k(t)$ as $k \to \infty$ is given in (A.24).

A simplified expression for the prefactor $a(x_0, x_0, t)$ in (6.4a) can be obtained from (6.3b) if we use the definition of $x_0(t)$, i.e., $v(x_0) = 2/t$. The result is

$$a(x_0, x_0, t) = [v'(x_0)]^{-2}[8/3t - v(2x_0)] \tag{6.4b}$$

We remark that, for monodisperse initial conditions, Eqs. (6.4a), (6.4b) agree with the previous result (5.2), since in this case $a(x_0, x_0, t)$ is equal to $C(t)$ in (5.3c).

6.3. The Scaling Limit

First we consider the scaling behavior of the generating function $H(x, y, t)$ in (6.3). As a definition for the "average cluster size" we choose again the weight-average cluster size, i.e.,

$$s(t) = M_2(t)/M_1(t) \sim t \qquad (t \to \infty) \tag{6.5}$$

The behavior in the scaling limit of the generating functions $F(x, t)$ and $(\partial F/\partial x)(x, t)$ is given in Appendix A. From (A.26) it follows that the factors $(\partial F/\partial x)(x, t)$ and $(\partial F/\partial y)(y, t)$ in (6.3a) approach a scale-invariant form in terms of the scaling variables $\rho_1 = -xs(t)$ and $\rho_2 = -ys(t)$, as in (4.15), but now with a different scaling function $\psi(\rho) = 4/(2 + \rho)^2$. A scaling form for $H(x, y, t)$ is obtained if we expand $a(x, y, t)$ in (6.3b) about $x = y = 0$ and take into account only the leading order in the scaling variables ρ_1 and ρ_2. The result is

$$H(x, y, t) \xrightarrow{S} -s(t)^{-1} \rho_1 \rho_2 [1 + \tfrac{1}{4}(\rho_1 + \rho_2) + \tfrac{1}{12} \rho_1 \rho_2] \psi(\rho_1) \psi(\rho_2) \tag{6.6}$$

This shows that the generating function $H(x, y, t)$ approaches a *scale-invariant form* in the scaling limit, *independent* of the initial distribution $c_k(0)$.

Equation (6.6) can readily be inverted to yield the scaling behavior of the factorial cumulants $e_{mn}(t)$. The simplest way to do this is as follows. Consider the explicit form (5.2), (5.3) of $e_{mn}(t)$, which was derived for monodisperse initial conditions. In the scaling limit, Eq. (5.2) reduces to the following scaling form in terms of the scaling arguments $r_1 = m/s(t)$ and $r_2 = n/s(t)$:

$$e_{mn}(t) \xrightarrow{S} s(t)^{-3}\, \Phi(r_1, r_2) \tag{6.7a}$$

with the scaling function $\Phi(r_1, r_2)$ given by

$$\Phi(r_1, r_2) = -\tfrac{1}{3}[1 - (r_1 + r_2) + 4r_1 r_2]\, \varphi(r_1)\, \varphi(r_2) \tag{6.7b}$$

Here $\varphi(r) = 4e^{-2r}$ is the scaling function for the concentrations $c_k(t)$ [see (A.17a) and (A.27)]. It can readily be verified that the scaling form (6.7a), (6.7b) for $e_{mn}(t)$ leads to the behavior (6.6) for the generating function $H(x, y, t)$. Since we know that (6.6) holds *independently* of the initial conditions, we infer that the scaling form (6.7) is also valid for a general initial distribution $c_k(0)$. Finally, the scaling behavior of the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ follows directly from (2.16). The result again has the form (4.21a), (4.21b), but now with $\varphi(r)$ and $\Phi(r_1, r_2)$ given by (A.27) and (6.7b), respectively.

7. GENERAL HOMOGENEOUS KERNELS; GENERAL INITIAL CONDITIONS

Next we consider the large class of models corresponding to *homogeneous* kernels $K(i, j)$, i.e., reaction rates of the form (1.8a), (1.8b). For such kernels, the properties of the fluctuations cannot be calculated exactly. However, one can study the *asymptotic* behavior of the covariances of the fluctuations in various limits. Combination of these asymptotic results then gives an impression of the *global* behavior of the fluctuations.[3] The relevant results for the solutions $c_k(t)$ of the macroscopic law are given in Appendix A.3.

The plan of this section is as follows. We start from Eq. (2.17) for the factorial cumulants $e_{mn}(t)$, which, for a general kernel $K(i, j)$, can be written as

$$\dot{e}_{mn}(t) = J_{mn}(t) + J_{nm}(t) - K(m, n)\, c_m(t)\, c_n(t) \tag{7.1a}$$

[3] With the restriction that we do not consider the post-gel stage ($t > t_c$) of gelling models ($\lambda > 1$). See the footnote 2 in Section 1, and a remark in Appendix A.3.

with J_{mn} defined by

$$J_{mn}(t) \equiv \sum_{i+j=m} K(i, j)\, c_i e_{nj} - e_{mn} \sum_{i=1}^{\infty} K(m, i)\, c_i - c_m \sum_{j=1}^{\infty} K(m, j)\, e_{nj} \tag{7.1b}$$

From this equation we study first, for homogeneous kernels (1.8a)(1.8b), the asymptotic behavior of the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in the limit of large cluster sizes ($m, n \to \infty$) and, next, the result in the scaling limit. This is done in Sections 7.1 and 7.2, respectively.

7.1. Fluctuations at Large Cluster Sizes ($m, n \to \infty$)

From the exactly solvable models, we know [see (4.13), (6.4), and, in Ref. 1, (4.14)] that, for large cluster sizes, the factorial cumulants e_{mn} have the form $e_{mn} \sim C(t)\, mnc_m c_n$, where $C(t)$ is some function of time. Here we show that this asymptotic result is also consistent in general for homogeneous kernels of the form (1.8a), (1.8b).

In order to study the behavior of $e_{mn}(t)$ at large cluster sizes, it is convenient to introduce a new function $a_{mn}(t)$, defined by

$$e_{mn}(t) \equiv a_{mn}(t)\, c_m(t)\, c_n(t) \tag{7.2}$$

The known results from the exactly solvable models suggest the following Ansatz for the asymptotic behavior of a_{mn} for general homogeneous kernels:

$$a_{mn}(t) \sim m b_n(t) \qquad (m \to \infty) \tag{7.3a}$$

$$b_n(t) \sim C(t)\, n \qquad (n \to \infty) \tag{7.3b}$$

In addition we assume that the limits $m \to \infty$ and $n \to \infty$ can be interchanged, so that, e.g., in the limit $m, n \to \infty$ with m/n fixed it holds that $a_{mn} \sim C(t)\, mn$. In general, $b_n(t)$ and $C(t)$ in (7.3a), (7.3b) will depend on the initial conditions.

In order to verify the Ansatz (7.3a), (7.3b), we estimate first the relative magnitude of the various terms in (7.1a) as $m, n \to \infty$. We start with the *left-hand side* of (7.1a). From Appendix A.3 we recall that $\dot{c}_k \sim k\dot{z}c_k$ as $k \to \infty$, with $\dot{z}(t) > 0$. As a result the dominant contribution to $\dot{e}_{mn}$ in (7.1a) is $a_{mn}(\dot{c}_m c_n + c_m \dot{c}_n)$, so that for large m and n the left-hand side of Eq. (7.1a) is given by

$$\begin{aligned} \text{LHS(7.1a)} &\sim e_{mn}(\dot{c}_m/c_m + \dot{c}_n/c_n) \\ &\sim (m+n)\, \dot{z} e_{mn} \qquad (m, n \to \infty) \end{aligned} \tag{7.4}$$

Next we consider the *right-hand side* of (7.1a). The last term, i.e., $K(m, n)\, c_m c_n$, is at most of the order of e_{mn} as $m, n \to \infty$, which is negligibly small compared to the left-hand side of (7.1a). Similarly, the last term on the right in (7.1b) is at most of the order of e_{mn}, and can be neglected. Consequently one finds that, for large m and n, the right-hand side of (7.1a) reduces to

$$\begin{aligned} \mathrm{RHS}(7.1\mathrm{a}) &\sim J_{mn} + J_{nm} \\ &\sim e_{mn}(T_{mn}/c_m + T_{nm}/c_n) \qquad (m, n \to \infty) \end{aligned} \tag{7.5a}$$

where $T_{mn}(t)$ is defined as

$$T_{mn}(t) \equiv \sum_{i+j=m} K(i, j)\, c_i c_j a_{nj}/a_{mn} - c_m \sum_{j=1}^{\infty} K(m, i)\, c_i \tag{7.5b}$$

Our task, therefore, is to show that, for a_{mn} as in (7.3a), (7.3b), Eqs. (7.4) and (7.5) yield the same results.

Consider $T_{mn}(t)$ in (7.5b). For large values of n, the factor a_{nj}/a_{mn} in (7.5b) reduces to b_j/b_m, due to our assumption (7.3a). The dominant contribution to the first term on the right in (7.5b) comes from large j values. For large j and m, the factor b_j/b_m reduces to j/m, which can be replaced with $\frac{1}{2}(i+j)/m = \frac{1}{2}$. It follows that $T_{mn}(t) \sim \dot{c}_m(t)$ as $m, n \to \infty$, and, similarly, $T_{nm}(t) \sim \dot{c}_n(t)$. Substitution of these results into (7.5a) and comparison with (7.4) shows that, for large m and n, both sides of Eq. (7.1) are *identical*. From this result we conclude that for all homogeneous kernels of the form (1.8), *the Ansatz (7.3) is consistent*. The time dependence of $b_n(t)$ and of $C(t)$ remains undetermined.

7.2. The Scaling Limit

A second limit in which $e_{mn}(t)$ assumes a simple, universal form is the *scaling limit*, where the average cluster size diverges: $s(t) \to \infty$ and $m, n \to \infty$, with the scaling arguments $r_1 \equiv m/s(t)$ and $r_2 \equiv n/s(t)$ fixed.

From Appendix A we know that, in the scaling limit (S), the concentrations $c_k(t)$ approach a scale-invariant form, characterized by a scaling function $\varphi(r)$:

$$c_k(t) \xrightarrow{\mathrm{S}} s(t)^{-\tau'} \varphi(r); \qquad r \equiv k/s(t) \tag{7.6}$$

where $\tau' = \frac{1}{2}(\lambda + 3)$ for gelling models and $\tau' = 2$ for nongelling models. In this section we show that the factorial cumulants $e_{mn}(t)$ also assume a scaling form, as follows:

$$e_{mn}(t) \xrightarrow{\mathrm{S}} s(t)^{-\zeta} \Phi(r_1, r_2) \tag{7.7}$$

where the value of the exponent ζ is different for gelling and nongelling models. We note that $\Phi(r_1, r_2)$ in (7.7) is a *symmetric* function of the scaling arguments r_1 and r_2. Furthermore, the *sign* of $\Phi(r_1, r_2)$ may be different for different values of r_1 and r_2. An example where $\Phi(r_1, r_2)$ does not have a definite sign is the scaling function (6.7b) for the model $K_{ij} = 1$. In this case $\Phi(r_1, r_2)$ is *positive* if $r_1 < \frac{1}{4}$ and $r_2 > (1 - r_1)/(1 - 4r_1)$, or $r_2 < \frac{1}{4}$ and $r_1 > (1 - r_2)/(1 - 4r_2)$, and *negative* (or zero) for all other values of r_1 and r_2.

The value of the exponent ζ in (7.7) can be determined from the relation (2.19b) for $e_{mn}(t)$, i.e., $\sum_n n e_{mn} = -m c_m$. Substitution of the scaling forms (7.6) and (7.7) into (2.19b) gives

$$s(t)^{2-\zeta} \int_0^\infty dy\, y\Phi(r_1, y) = -s(t)^{1-\tau'} r_1 \varphi(r_1) \tag{7.8}$$

Comparison of powers of $s(t)$ in (7.8) shows that ζ is related in a very simple way to the exponent τ' in (7.6), namely

$$\zeta = \tau' + 1 \tag{7.9}$$

As a consequence, one finds that $\zeta = \frac{1}{2}(\lambda + 5)$ for gelling systems (which correspond to $\lambda > 1$) and $\zeta = 3$ for nongelling systems ($\lambda \leqslant 1$). Moreover, one obtains a relation between the scaling functions $\Phi(r_1, r_2)$ and $\varphi(r)$,

$$\int_0^\infty dy\, y\Phi(r, y) = \int_0^\infty dy\, y\Phi(y, r) = -r\varphi(r) \tag{7.10}$$

where we used the symmetry of $\Phi(r_1, r_2)$. In the derivation of (7.9) and (7.10) it is assumed that the integrals in (7.10) converge. For the exactly soluble models $K_{ij} = i + j$ and $K_{ij} = 1$ discussed in this paper, and $K_{ij} = ij$ discussed in Ref. 1, this assumption can readily be verified.

As an immediate consequence of the scaling law (7.7) for $e_{mn}(t)$, with ζ given by (7.9), one finds that the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$, which are related to e_{mn} by (2.16), also assume a scale-invariant form in the scaling limit, as follows:

$$\langle\langle \xi_m \xi_n \rangle\rangle \xrightarrow{S} s(t)^{-\zeta} \Psi(r_1, r_2) \tag{7.11a}$$

with

$$\Psi(r_1, r_2) = \delta(r_1 - r_2)\, \varphi(r_2) + \Phi(r_1, r_2) \tag{7.11b}$$

In the derivation of (7.11) we used that, in the scaling limit, the Kronecker delta in (2.16) assumes the form $s(t)^{-1}\, \delta(r_1 - r_2)$.

An equation for $\Phi(r_1, r_2)$ is obtained if we substitute the Ansatz (7.7) into Eq. (7.1). We consider the left-hand side and the right-hand side of (7.1a) separately. Substitution of (7.7) into the left-hand side gives

$$\text{LHS(7.1a)} \xrightarrow{\text{S}} -\dot{s}s^{-1-\zeta}\left(\zeta\Phi + r_1\frac{\partial\Phi}{\partial r_1} + r_2\frac{\partial\Phi}{\partial r_2}\right) \tag{7.12}$$

Similarly, we find for the right-hand side of (7.1a)

$$\begin{aligned}\text{RHS(7.1a)} \xrightarrow{\text{S}} s^{1+\lambda-\tau'-\zeta}\{&\lim_{\varepsilon\downarrow 0}[I_\varepsilon(r_1, r_2) + I_\varepsilon(r_2, r_1)] \\ &- K(r_1, r_2)\,\varphi(r_1)\,\varphi(r_2)\}\end{aligned} \tag{7.13a}$$

where we have defined

$$\begin{aligned}I_\varepsilon(r_1, r_2) \equiv &\int_{\varepsilon r_1}^{(1-\varepsilon)r_1} dy\, K(y, r_1 - y)\,\varphi(y)\,\Phi(r_2, r_1 - y) \\ &- \Phi(r_1, r_2)\int_{\varepsilon r_1}^{\infty} dy\, K(r_1, y)\,\varphi(y) \\ &- \varphi(r_1)\int_{\varepsilon r_1}^{\infty} dy\, K(r_1, y)\,\Phi(r_2, y)\end{aligned} \tag{7.13b}$$

We introduced the ε limit in (7.13a) in order to avoid divergences occurring in the individual integrals for $\varepsilon = 0$. Combination of Eqs. (7.12) and (7.13a) and use of (A.31a) for $\dot{s}(t)$ shows that $\Phi(r_1, r_2)$ satisfies the following linear, inhomogeneous, integrodifferential equation:

$$\begin{aligned}-w&\left(\zeta\Phi + r_1\frac{\partial\Phi}{\partial r_1} + r_2\frac{\partial\Phi}{\partial r_2}\right) \\ &= \lim_{\varepsilon\downarrow 0}[I_\varepsilon(r_1, r_2) + I_\varepsilon(r_2, r_1)] - K(r_1, r_2)\,\varphi(r_1)\,\varphi(r_2)\end{aligned} \tag{7.14}$$

where the value of ζ is given in (7.9).

Equation (7.14) for $\Phi(r_1, r_2)$ cannot be solved *exactly* for general kernels $K(r_1, r_2)$. However, one can study the *asymptotic* behavior of $\Phi(r_1, r_2)$ for large and small values of r_1 and r_2. The detailed behavior of $\Phi(r_1, r_2)$ for *small* values of r_1 and r_2 is complicated and rather diverse, and will not be discussed here. The behavior of $\Phi(r_1, r_2)$ at *large* values of r_1 and r_2 is fortunately very simple. If we define $\alpha(r_1, r_2)$ by

$$\Phi(r_1, r_2) \equiv \alpha(r_1, r_2)\,\varphi(r_1)\,\varphi(r_2) \tag{7.15}$$

then one can show, along the same lines as in Section 7.1, that the behavior of $\alpha(r_1, r_2)$ for large values of r_1 and r_2 is given by

$$\alpha(r_1, r_2) \sim r_1 \beta(r_2) \qquad (r_1 \to \infty) \tag{7.16a}$$

with

$$\beta(r_2) \sim \gamma r_2 \qquad (r_2 \to \infty) \tag{7.16b}$$

Clearly, Eqs. (7.15), (7.16a), and (7.16b) are the analog in the scaling limit of the behavior (7.2), (7.3a), and (7.3b) at large cluster sizes. This shows that the results from the scaling theory are in agreement with the behavior in the limit $m, n \to \infty$, i.e., that both limits have overlapping regions of validity.

8. DISCUSSION AND SUMMARY

In this paper we applied van Kampen's Ω-expansion to a master equation describing coagulation in finite, spatially homogeneous systems. From the leading order in the expansion we find that the concentrations $c_k(t)$ satisfy the macroscopic law (1.4), which is known as Smoluchowski's coagulation equation. The next order in the expansion yields a linear Fokker–Planck equation for the probability density $\Pi(\xi, t)$ of the fluctuations $\xi = (\xi_1, \xi_2, \ldots)$ in the numbers of clusters of size $k = 1, 2, \ldots$. The solution of the Fokker–Planck equation is completely determined by the covariance matrix of the fluctuations, i.e., $\Xi_{mn} = \langle\langle \xi_m \xi_n \rangle\rangle$.

We start the discussion with some critical comments on the *method* of this paper. We recall[1,2] that the validity of the Gaussian approximation, and hence of the Fokker–Planck approach, has been proved by Kurtz[21] for a *finite* number of reactants and a *fixed* time interval $[0, T]$. Obviously, this result is not applicable to the models considered in this paper, since in our case the number of reactants, i.e., the number of variables ξ_k, is *infinitely large*. Nevertheless, Kurtz's proof is of interest, since it demonstrates very clearly the limitations of our approach: the predictions from the Fokker–Planck equation are inaccurate at large cluster sizes ($k \gtrsim k_M$) and at large times ($t \gtrsim t_M$), where the cluster size k_M and the time t_M depend upon the size of the system. The consequences of these inaccuracies will be discussed first for large cluster sizes and then for large times.

The limitations of our approach at extremely large cluster sizes ($k > M$) are obvious. In the master equation such clusters cannot occur, whereas in the Fokker–Planck equation their occurrence is not excluded *a priori*. As a result, the *moments* of m_k ($k = 1, 2, \ldots$), as described in the

Fokker–Planck approach, also contain contributions from unphysically large clusters, of size $k > M$:

$$\sum_{k=1}^{M} k^{\alpha} m_k \simeq M\left(\sum_{k=1}^{\infty} k^{\alpha} c_k\right) + M^{1/2}\left(\sum_{k=1}^{\infty} k^{\alpha} \xi_k\right) + \cdots \tag{8.1}$$

Fortunately, the contributions on the right-hand side from clusters of size $k > M$ are *exponentially small*, of the order of $c_M(t)$, much smaller therefore than the error made in neglecting the terms of order $M^{-1/2}$ in the expansion of the master equation, i.e., Eq. (2.5). This justifies *a posteriori* the introduction of additional variables c_k and ξ_k with $k > M$.

More seriously, the Gaussian (or Fokker–Planck) approximation breaks down if the predicted number of k-mers, i.e.,

$$\langle m_k \rangle \simeq M c_k(t) \tag{8.2a}$$

is of the order of unity. As a result of (A.28), this happens if the cluster size k is of the order of $k_M(t) \equiv |z(t)|^{-1} \log M$. For such clusters the size of the fluctuations in m_k is given by

$$\ll m_k^2 \gg^{1/2} \simeq (M \ll \xi_k^2 \gg)^{1/2} \simeq [M c_k(t)]^{1/2} \tag{8.2b}$$

which is of the *same* order of magnitude as the average value $\langle m_k \rangle$ in (8.2a). It follows that the Gaussian approximation is invalid if $k \gtrsim k_M(t)$. However, the contribution of clusters of size $k \gtrsim k_M(t)$ to the moments $\sum_k k^{\alpha} m_k$ in (8.1) is of relative order M^{-1}, and hence negligibly small compared to the fluctuations, which are of relative order $M^{-1/2}$. We conclude that, although our description of large clusters, of size $k \gtrsim k_M(t)$, is inadequate, the error made is negligibly small. A further conclusion is that the result (8.1), which is accurate to relative order $M^{-1/2}$, *cannot* be improved by taking into account higher order terms in the Ω-expansion (2.5). This can be seen from (8.2). Equation (8.2) shows that, in our case, the Ω-expansion is *not* an asymptotic expansion in powers of the inverse system size M^{-1}, but rather, for each cluster size k, an expansion in terms of $[Mc_k(t)]^{-1}$. Thus, higher powers of M^{-1} in (2.5) correspond to higher powers of $[Mc_k(t)]^{-1}$ in (8.2), and any finite number of terms in this expansion is inadequate for clusters of size $k \simeq k_M(t)$, where $[Mc_k(t)]^{-1} \simeq 1$. As a consequence, the error in (8.1) is always of relative order M^{-1}. This argument shows that in our case the Ω-expansion is *not* what it usually is[2]: a systematic expansion in powers of a small parameter.

Next we show that the fluctuations become important *at large times* in nongelling models and *near the gelpoint* in gelling models. For this purpose

we consider again the moments $\sum_k k^\alpha m_k$ introduced in (8.1). As a measure for the relative magnitude of the fluctuations, we consider the ratio

$$R(t) \equiv \left\langle\!\!\left\langle \left(\sum_k k^\alpha m_k \right)^2 \right\rangle\!\!\right\rangle \Big/ \left(\sum_k k^\alpha \langle m_k \rangle \right)^2 \tag{8.3}$$

For large M, the value of $R(t)$ can be expressed in terms of the concentrations c_k and the fluctuations ξ_k as follows:

$$R(t) \sim M^{-1} \sum_{k,l} k^\alpha l^\alpha \ll \xi_k \xi_l \gg / (M_\alpha)^2 \tag{8.4}$$

where $M_\alpha(t)$ is the αth moment of $c_k(t)$. Thus, $R(t)$ is always small, of the order of M^{-1}, as $M \to \infty$ with the time t kept fixed. However, for a fixed value of M, $R(t)$ becomes large in the scaling limit, where the average cluster size diverges $[s(t) \to \infty]$. With the use of the scaling behavior (7.11) for $\ll \xi_k \xi_l \gg$ and (A.30) for $c_k(t)$, we find that for large values of $s(t)$, Eq. (8.4) reduces to

$$R(t) \sim C_\alpha M^{-1} [s(t)]^{\tau' - 1} \qquad [s(t) \to \infty] \tag{8.5}$$

where C_α is some constant. In the derivation of (8.5) we have approximated the sums in (8.4) by integrals, which is allowed if $\alpha > \tau' - 1$. The fluctuations in the moment $\sum_k k^\alpha m_k$ become important as soon as $R(t) \gtrsim 1$. According to (8.5), this happens if $t \gtrsim t_M$, where the time t_M is defined by

$$s(t_M) \equiv M^{1/(\tau' - 1)} \tag{8.6}$$

We conclude that for $t \gtrsim t_M$ the fluctuations are not small, so that the Fokker–Planck approach becomes invalid. From a physical point of view, the importance of the fluctuations at $t \simeq t_M$ is quite obvious. The main contribution to (8.5) comes from large clusters, of size $k \gtrsim s(t)$, and the number of such clusters is small, of the order of unity, for $t \simeq t_M$. This can be seen from (A.30).

We specify the result (8.6) for gelling and nongelling models, respectively. In *gelling models*, which correspond to $\lambda > 1$ in (1.8a), we know from Appendix A that $\tau' = \frac{1}{2}(\lambda + 3)$. Moreover, it follows from Eq. (A.31a) that $s(t)$ diverges proportional to $(t_c - t)^{-2/(\lambda - 1)}$ as $t \uparrow t_c$. As a consequence we find that the fluctuations in gelling models become important if $t \simeq t_M$, where t_M lies very close to the gelpoint t_c:

$$(t_c - t_M) \simeq M^{-(\lambda - 1)/(\lambda + 1)} \qquad (\lambda > 1) \tag{8.7a}$$

In *nongelling systems* ($\lambda \leqslant 1$), where $\tau' = 2$, it follows from (8.6) that

fluctuations become important if $t \simeq t_M$, with $s(t_M) = M$. For models with $\lambda < 1$, this corresponds to

$$t_M \simeq M^{1-\lambda} \qquad (\lambda < 1) \tag{8.7b}$$

due to (A.31a). The results for nongelling models with $\lambda = 1$ are slightly more complicated. One finds that $t_M \simeq \log M$ if $\lambda = 1$ and $\mu = 0$, and $t_M \simeq (\log M)^2$ if $\lambda = 1$ and $\mu > 0$.[13]

Next we discuss the relationship between the probability distribution $P(\mathbf{m}, t)$ in the master equation and the probability density $\Pi(\xi, t)$ in the Fokker–Planck equation. From the discussion of large cluster sizes it will be clear that $P(\mathbf{m}, t)$ and $\Pi(\xi, t)$ are *not* simply identical or proportional. The correspondence between them is more complicated. Since the discrepancy between the results from the master equation and the Fokker–Planck approach becomes apparent only at large cluster sizes, it is natural to sum over the large clusters in order to obtain a description in terms of small clusters only. For this reason we consider the marginal probability density $\Pi_r(\xi^{(r)}, t)$, which is defined as

$$\Pi_r(\xi^{(r)}, t) \equiv \int \prod_{j>r} d\xi_j \, \Pi(\xi, t) \tag{8.8a}$$

and compare it to the marginal probability $P_r(\mathbf{m}^{(r)}, t)$ that the numbers of clusters of size $k \leqslant r$ are given by $\mathbf{m}^{(r)} = (m_1, \ldots, m_r)$, i.e.,

$$P_r(\mathbf{m}^{(r)}, t) \equiv \sum_{\{m_k; k>r\}} P(\mathbf{m}, t) \tag{8.8b}$$

The relationship between $P_r(\mathbf{m}^{(r)}, t)$ and $\Pi_r(\xi^{(r)}, t)$ for large M is simply given by

$$P_r(\mathbf{m}^{(r)}, t) = M^{-r/2} \Pi_r(\xi^{(r)}, t) + \cdots \qquad (M \to \infty) \tag{8.9}$$

Possible correction terms on the right-hand side are of relative order $M^{-1/2}$ as $M \to \infty$. The factor $M^{-r/2}$ guarantees that $\Pi_r(\xi^{(r)}, t)$ is properly normalized. In conclusion: the relation between $P(\mathbf{m}, t)$ and $\Pi(\xi, t)$ is that for each finite value of r, the marginal probability distributions are related by (8.9) as $M \to \infty$. We remark that Eq. (8.9) represents a generalization of Kurtz's theorem to systems with an infinite number of reactants. It would be of interest if this result from the Ω-expansion could be proved rigorously.

The role of the *factorial cumulants* $e_{mn}(t)$ in this paper is more complicated than in Ref. 1. For $K_{ij} = ij$ we found[1] that e_{mn} reflects the influence of the conservation law for the total mass, $\sum_k k m_k = M$. The same con-

clusion holds for the model $K_{ij} = i + j$ considered in this paper. The interpretation of $e_{mn}(t)$ for $K_{ij} = i + j$ is particularly clear in the exact solution[5] of the master equation with a monodisperse initial condition. The exact solution shows that $P(\mathbf{m}, t)$ is a product of Poisson distributions for the occupation numbers m_k and a Kronecker delta representing mass conservation. Without the Kronecker delta, the factorial cumulants would vanish. Hence $e_{mn}(t)$ can be interpreted, also for $K_{ij} = i + j$, as a reflection of the conservation law for the total mass. The fact that $e_{mn}(t)$ is *negative* (sub-Poisson statistics) for all m and n and all $t > 0$ simply means that an excess of m-mers implies that, most likely, there will be fewer n-mers, i.e., $\langle \xi_n \rangle < 0$. For general initial conditions the exact solution of the master equation (1.1) is not known, and the argument given above for monodisperse initial conditions breaks down. Nevertheless, one finds that the sign of e_{mn} is negative in the limit of large cluster sizes and in the scaling limit. This can be seen from Eqs. (4.13) and (4.20), respectively. Note that the factor $H(x_1^s, x_1^s, 0)$ in (4.13) is negative. This follows from (4.1), (4.2b), and the fact that x_1^s is positive.

The interpretation of the factorial cumulants $e_{mn}(t)$ for the model $K_{ij} = 1$ is more difficult. The exact solution of Bayewitz *et al.*[4] is not simply a product of Poisson distributions for m_k multiplied with a Kronecker delta for the total mass. Hence it is not obvious that the factorial cumulants should be negative, and in fact we know from Section 5.1 that $e_{mn}(t)$ may be *positive* for some combinations of m, n, and t. An explanation for this phenomenon is given in Section 5.2. Qualitatively, the same explanation applies for $K_{ij} = 1$ and *general* initial conditions. This follows from the fact that $e_{mn}(t)$ becomes independent of the initial conditions in the scaling limit, as demonstrated by Eq. (6.7). A simple interpretation of $e_{mn}(t)$ for general homogeneous kernels has not been found.

At the level of the macroscopic law there exists a mapping[22] between the two exactly soluble models $K_{ij} = i + j$ and $K_{ij} = ij$. The mapping can be formulated as follows: if $c_k(t)$ is the solution of Smoluchowski's equation with the initial condition $c_k(0)$ and rate constants $K_{ij} = i + j$, then

$$\bar{c}_k(t) = k^{-1} c_k(t^*)/M_0(t^*) \tag{8.10}$$

with $M_0(t) = \sum_k c_k(t)$ and $t^* = -\log[1 - t/M_0(0)]$ is the solution for $K_{ij} = ij$ and $\bar{c}_k(0) = k^{-1} c_k(0)/M_0(0)$. As a result of (8.10), the conservation law (2.19b) immediately implies that there also exists a relation between the factorial cumulants in the two models, namely

$$\sum_n n\bar{e}_{mn}(t) = m^{-1} \sum_n n e_{mn}(t^*)/M_0(t^*) \tag{8.11}$$

However, it can be shown with the use of the generating functions of $\bar{e}_{mn}$ and e_{mn} that a more detailed relation between these cumulants does not exist. Thus, it appears that a simple mapping between both models is possible *only* at the level of the macroscopic law.

A particularly simple form for the factorial cumulants e_{mn} was found for the models $K_{ij} = i + j$ and $K_{ij} = ij$ (with $t < t_c$; see Ref. 1) if the initial conditions are monodisperse. In this case $e_{mn}(t)$ assumes the form

$$e_{mn}(t) = -mnc_m(t)\, c_n(t)/M_2(t) \tag{8.12}$$

The factor $[M_2(t)]^{-1}$ guarantees that e_{mn} satisfies Eq. (2.19b). Which other kernels lead to the simple form (8.12) for e_{mn}? This question is investigated in Appendix B. We find that (8.12) is an *exact* solution of Eq. (2.17), with a monodisperse initial condition, for all kernels K_{ij} that are *linear* in the following sense:

$$K_{ij} = iB_j + jB_i \tag{8.13}$$

The constants B_j in (8.13) satisfy the restriction $B_j/j \leqslant \text{const}$ as $j \to \infty$. For all linear models (8.13), it can be shown[20] that the probability distribution $\Pi(\xi, t)$ is given by (3.5) if e^t is replaced with $(M_2)^{1/2}$. Furthermore, if for large values of j, B_j is homogeneous ($B_j \sim j^{\lambda-1}$), then $e_{mn}(t)$ approaches a scaling form in the scaling limit, with the scaling function $\Phi(r_1, r_2)$ given by

$$\Phi(r_1, r_2) = -r_1 r_2 \varphi(r_1)\, \varphi(r_2) \Big/ \int_0^\infty dy\, y^2 \varphi(y) \tag{8.14}$$

Here $\varphi(r)$ is the scaling function for $c_k(t)$; see (7.6). The interpretation of the factorial cumulants given for $K_{ij} = i + j$ and $K_{ij} = ij$ is in general valid for *all* linear models (with the restriction $t < t_c$ in gelling models). In all cases the fluctuations obey sub-Poisson statistics.

From a physical point of view, one of the most interesting phenomena encountered in this paper is the *scaling behavior* of the fluctuations for general homogeneous kernels (see Section 7). It is of interest to consider possible extensions of this behavior to other fields and experimental verification. We mention two possible applications. The first is *percolation theory*. For instance, in Monte Carlo simulations of bond percolation, one starts[23] from a large but finite lattice with M sites and considers the numbers $m_k(p)$ of clusters of size k, where p is the probability that a bond has formed. In these simulations one observes[23] that the concentrations $c_k(p) \equiv m_k(p)/M$ approach a scale-invariant form, very similar to (7.6), near the critical point p_c. This phenomenon is observed also in the case of site percolation.

Thus, there is a complete analogy between the scaling behavior in percolation theory and in the present mean field approach, at least at the macroscopic level. For this reason we expect that scaling behavior of the fluctuations also occurs in percolating systems near their critical point. It would be interesting if this conjecture could be proved or disproved. A second field where the scaling law (7.7) could be tested is computer simulation of *cluster–cluster aggregation processes*. In this case the scaling behavior of the concentrations has been demonstrated by Meakin *et al.*[24] It would be of interest if the present scaling theory for the fluctuations could be verified experimentally in such systems.

Before closing this paper, we summarize the main results. We have studied the properties of the fluctuations for a large class of coagulation models that includes most models used in the literature.[8,9] Special attention has been paid to two exactly soluble models, corresponding to the choices $K_{ij} = i + j$ and $K_{ij} = 1$ for the rate constants in the master equation (1.1). For these models and *monodisperse initial conditions*, we obtained explicit results for the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$, for the probability distribution $\Pi(\xi, t)$, and for the two-time correlation functions $\langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle$. For *general initial conditions* we found an exact expression for the generating function of the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$. From this exact expression we calculated the asymptotic behavior of $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ at large cluster sizes $(m, n \to \infty)$ and in the scaling limit. With the use of these results for the models $K_{ij} = i + j$ and $K_{ij} = 1$ and the results for $K_{ij} = ij$,[1] it was possible to determine the asymptotic behavior of the covariances for *general homogeneous kernels* of the form (1.8). One finds that the factorial cumulants $e_{mn}(t)$, which are related to the covariances as $e_{mn} = \langle\langle \xi_m \xi_n \rangle\rangle - \delta_{mn} c_n$, are given for large values of m and n by $e_{mn} \sim C(t)\, mnc_m c_n$. Furthermore, we found a novel scaling behavior of the fluctuations in the scaling limit, where the average cluster size $s(t)$ diverges. In this limit e_{mn} approaches a scale-invariant form, as follows:

$$e_{mn} \xrightarrow{S} s(t)^{-\zeta}\, \Phi(m/s(t), n/s(t))$$

The exponent ζ is related in a simple way to the degree of homogeneity of the rate constants, namely $\zeta = 3$ for nongelling models $(\lambda \leqslant 1)$ and $\zeta = \frac{1}{2}(\lambda + 5)$ for gelling models $(\lambda > 1)$. We also derived an equation for the scaling function $\Phi(r_1, r_2)$ and we determined its shape at large values of r_1 and r_2.

APPENDIX A

In this Appendix we summarize some relevant results for the solutions $c_k(t)$ of the macroscopic law (1.4). We discuss first the results for the

models $K_{ij}=i+j$ and $K_{ij}=1$, and then some results for general homogeneous kernels of the form (1.8). The models $K_{ij}=i+j$ and $K_{ij}=1$ have been solved for general initial conditions by Golovin[14] and Melzak,[15] respectively, but we have chosen a slightly different presentation that is better suited for our purposes. The results for general homogeneous kernels are taken from Refs. 13, 17, and 18.

A1. $K_{ij}=i+j$

We start with the model $K_{ij}=i+j$, for which Smoluchowski's equation takes the form

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} (i+j)\, c_i c_j - (kM_0 + 1)\, c_k \tag{A.1}$$

Here M_0 is the *zeroth moment* of $c_k(t)$. In general, the nth moment $M_n(t)$ of the cluster size distribution is defined as

$$M_n(t) = \sum_{k=1}^{\infty} k^n c_k(t) \tag{A.2}$$

and the first few moments can readily be calculated from (A.1) as

$$M_0(t) = M_0(0)\, e^{-t}; \qquad M_1(t) = 1; \qquad M_2(t) = M_2(0)\, e^{2t} \tag{A.3}$$

From the fact that the sol mass $M_1(t)$ is conserved for all $t \geqslant 0$ we infer that for $K_{ij}=i+j$, gel formation does not occur, i.e., that this model is a *non-gelling model.*

In order to solve Eq. (A.1) for general initial conditions, we introduce the generating functions

$$f(x,t) = \sum_{k=1}^{\infty} c_k(t)\, e^{kx}; \qquad F(x,t) = \sum_{k=1}^{\infty} c_k(t)(e^{kx} - 1) \tag{A.4}$$

An equation for $f(x,t)$ is obtained if we multiply (A.1) with e^{kx} and sum over all k. The result is

$$\frac{\partial f}{\partial t} = (f - M_0)\frac{\partial f}{\partial x} - f \tag{A.5}$$

Subtraction from (A.5) of the equation for the zeroth moment, i.e., $\dot{M}_0 = -M_0$, gives

$$\frac{\partial F}{\partial t} = F\left(\frac{\partial F}{\partial x} - 1\right) \tag{A.6}$$

Equation (A.6) can be solved with the method of characteristics. As a result one finds that $F(x, t)$ is implicitly determined by

$$F(x, t) = e^{-t}u(z); \qquad z(x, t) \equiv F(x, t) - x \tag{A.7}$$

The function $u(x)$ in (A.7) is determined by the initial condition $v(x) = F(x, 0)$. In Sections 3 and 4 we also need an expression for the partial derivative $\partial F/\partial x$ of $F(x, t)$. Differentiation of (A.7) with respect to x gives

$$\frac{\partial F}{\partial x}(x, t) = \frac{u'(z)}{u'(z) - e^t} \tag{A.8}$$

It follows from the definition (A.4) that $\partial f/\partial x$ is also equal to the right-hand side of (A.8).

For the special case of *monodisperse initial conditions*, $c_k(0) = \delta_{k1}$, the concentrations $c_k(t)$ can be calculated explicitly. In this case the initial condition is $v(x) = F(x, 0) = e^x - 1$. As a consequence one finds from (A.7) that

$$x = F - z = F - e^t F + \log(1 + e^t F) \tag{A.9a}$$

or, in terms of $f(x, t)$,

$$x = f - e^t f + \log(e^t f) + 1 - e^{-t} \tag{A.9b}$$

In general the concentrations $c_k(t)$ can be calculated from the following contour integral:

$$kc_k(t) = \frac{1}{2\pi i} \oint \frac{dy}{y^{k+1}} \frac{\partial f}{\partial x}(x, t) = \frac{1}{2\pi i} \oint \frac{df}{y^k} \tag{A.10}$$

where we have defined $y \equiv e^x$. The integration path in (A.10) circles the origin $y = 0$ once in the counterclockwise direction. For monodisperse initial conditions we can use (A.9b) and the definition $y = e^x$ to calculate the integral in (A.10) explicitly. The result can be written as

$$c_k(t) = (1 - \tau) \frac{k^{k-1}}{\tau k!} (\tau e^{-\tau})^k \tag{A.11}$$

where we have introduced a new time variable $\tau(t) \equiv 1 - e^{-t}$.

We consider again the result (A.7) for *general initial conditions*. Equation (A.7) or (A.8) can be used to calculate the *asymptotic behavior* of the concentrations $c_k(t)$ in the limit of large cluster sizes ($k \to \infty$) and in the scaling limit [where $k \to \infty$, and the average cluster size $s(t) \to \infty$, with the ratio $k/s(t)$ fixed].

First we discuss the results in the limit $k \to \infty$. The large-k behavior of $c_k(t)$ can be calculated from the contour integral (A.10) with the use of the saddlepoint method.[16] It follows from (A.8) that the functions $x(f, t)$ and $y(f, t) = e^{x(f,t)}$ have a saddle point at $x_s(t)$ or $y_s(t)$, where x_s is implicitly determined by

$$u'(z_s) \equiv e^t; \qquad x_s \equiv F(x_s, t) - z_s = e^{-t} u(z_s) - z_s \tag{A.12}$$

and $y_s = e^{x_s}$. Accordingly, we choose the contour in (A.10) along the circle $f = f_s(t)\, e^{i\varphi}$, where f_s is defined by $f_s(t) \equiv f(x_s(t), t)$, and $-\pi < \varphi \leqslant \pi$. If we expand $x(f, t)$ in a Taylor series about $f = f_s$,

$$\begin{aligned} x(f, t) &= x_s(t) + \tfrac{1}{2}(f - f_s)^2\, e^{-t} u''(z_s) + \cdots \qquad (f \to f_s) \\ &= x_s(t) - \tfrac{1}{2}\varphi^2 e^{-t} u''(z_s) + \cdots \qquad (\varphi \to 0) \end{aligned} \tag{A.13}$$

and calculate the integral in (A.10) for large values of k, we obtain the following result for $c_k(t)$ as $k \to \infty$:

$$c_k(t) \sim [-2\pi e^{-t} u''(z_s)]^{-1/2}\, k^{-3/2} e^{-k x_s(t)} \qquad (k \to \infty) \tag{A.14}$$

Note that it follows from differentiation of (A.7) for $t = 0$ that $u''(z_s) < 0$.

Next we consider the scaling-limit (S), where the average cluster size diverges: $s(t) \to \infty$ and $k \to \infty$, with the ratio $k/s(t)$ fixed. As a definition of the "average cluster size" we choose $s(t) = M_2(t)$, but different choices for $s(t)$ would change only numerical values and not the essence of the results. In the scaling limit one finds from (A.7) that the generating function $F(x, t)$ approaches a scale-invariant form in terms of the scaling variable $\rho \equiv -x s(t)$ as follows:

$$F(x, t) \xrightarrow{\text{S}} -s(t)^{-1}[(1 + 2\rho)^{1/2} - 1] \tag{A.15}$$

Similarly, one finds a scaling function for the partial derivative $\partial F/\partial x$, namely

$$\frac{\partial F}{\partial x}(x, t) \xrightarrow{\text{S}} (1 + 2\rho)^{-1/2} \equiv \psi(\rho) \tag{A.16}$$

The scaling results (A.15) and (A.16) in terms of generating functions can readily be inverted to yield an expression for $c_k(t)$. One finds that

$$c_k(t) \xrightarrow{\text{S}} s(t)^{-2}\, \varphi(r); \qquad r \equiv k/s(t) \tag{A.17a}$$

where the scaling function $\varphi(r)$ is given by

$$\varphi(r) = (2\pi)^{-1/2}\, r^{-3/2} e^{-r/2} \tag{A.17b}$$

The results (A.15)–(A.17) obtained in the scaling limit do not depend on the initial conditions.

A2. $K_{ij}=1$

We start from Smoluchowski's equation for the model $K_{ij}=1$:

$$\dot{c}_k=\tfrac{1}{2}\sum_{i+j=k} c_i c_j - c_k M_0 \tag{A.18}$$

with M_0 defined in (A.2), and we introduce again the generating functions $f(x, t)$ and $F(x, t)$ defined in (A.4). For $F(x, t)$ one finds the following differential equation:

$$\partial F/\partial t=\tfrac{1}{2}F^2 \tag{A.19}$$

which is to be solved with the general initial condition $F(x, 0)\equiv v(x)$. The solution is

$$F(x, t)=v(x)/[1-\tfrac{1}{2}tv(x)] \tag{A.20}$$

We also need an expression for the x derivative of $F(x, t)$ or $f(x, t)$. From (A.20) one finds that

$$\frac{\partial F}{\partial x}(x, t)=\frac{\partial f}{\partial x}(x, t)=\frac{v'(x)}{[1-\tfrac{1}{2}tv(x)]^2} \tag{A.21}$$

Furthermore, the first few moments of $c_k(t)$ can readily be calculated from (A.18). The result is

$$M_0(t)=[\tfrac{1}{2}t+1/M_0(0)]^{-1}; \qquad M_1(t)=1; \qquad M_2(t)=M_2(0)+t \tag{A.22}$$

Since the sol mass is conserved for all times, we conclude that $K_{ij}=1$ is also a nongelling model.

An explicit result for the concentrations $c_k(t)$ can readily be found if the initial distribution is monodisperse, i.e., if $v(x)=e^x-1$. In this case calculation of the integral in (A.10) with $\partial F/\partial x$ given in (A.21) yields

$$c_k(t)=(1+t/2)^{-2}[t/(2+t)]^{k-1} \tag{A.23}$$

For this special case it follows from (A.22) that $M_0(t)=(1+t/2)^{-1}$ and $M_2(t)=1+t$.

We again consider Eq. (A.20) for general initial conditions. For general $c_k(0)$ it is not feasible to calculate $c_k(t)$ explicitly. However, one can calculate the *asymptotic* behavior of $c_k(t)$ for large cluster sizes and in the

scaling limit. The large-k behavior of $c_k(t)$ can be determined from (A.10) with $\partial f/\partial x$ given in (A.21). The dominant contribution to the integral in (A.10) as $k \to \infty$ comes from the pole at $x = x_0(t)$, where $x_0(t)$ is implicitly defined by $v(x_0) = 2/t$. Expansion of the integrand in (A.10) about $x_0(t)$ gives[16,17]

$$c_k(t) \sim 4[t^2 v'(x_0)]^{-1} e^{-kx_0} \qquad (k \to \infty) \tag{A.24}$$

Next we consider the scaling limit. In this case one finds from (A.20) that the generating function $F(x, t)$ approaches a scale-invariant form in terms of the scaling variable $\rho = -xs(t)$:

$$F(x, t) \xrightarrow{\text{S}} -s(t)^{-1}[2\rho/(2+\rho)] \tag{A.25}$$

In the derivation of (A.25) we have chosen $s(t) \equiv M_2(t)$, and we have used that $v(0) = 0$ and $v'(0) = 1$. Similarly, it follows from (A.21) that

$$\frac{\partial F}{\partial x}(x, t) \xrightarrow{\text{S}} \frac{4}{(2+\rho)^2} \tag{A.26}$$

The results (A.25) and (A.26) obtained in the scaling limit can readily be inverted to yield an expression for the cluster size distribution $c_k(t)$. One finds that $c_k(t)$ approaches a scaling form as in (A.17a), with $\varphi(r)$ given by

$$\varphi(r) = 4e^{-2r} \tag{A.27}$$

A different choice for the "average cluster size" $s(t)$ would change only the numerical values (length scales) in (A.25)–(A.27), and not the functional forms.

A3. General Homogeneous Kernels

Next we summarize some results concerning the asymptotic structure of solutions $c_k(t)$ of Smoluchowski's equation for homogeneous kernels of the form (1.8a), (1.8b).

We start with a comment on the possible occurrence of a gelation transition. It can be shown[13] that a gelation transition occurs if the degree of homogeneity in (1.8a) satisfies $\lambda > 1$ and is absent otherwise ($\lambda \leqslant 1$). The gelpoint t_c in gelling systems is characterized by a divergence of the moments $M_n(t)$, with $n \geqslant 2$, and by the onset of gel formation. In non-gelling systems the moments $M_n(t)$ remain finite and gel formation does not occur. In this paper we consider gelling systems only for $t < t_c$ and non-gelling systems for all times $t \geqslant 0$.

The large-k behavior of $c_k(t)$ has been calculated in Ref. 17 for homogeneous kernels with an exponent $\nu < 1$, and in Ref. 18 for kernels with $\nu = 1$. The definition of ν has been given in (1.8b). In all cases one finds that $c_k(t)$ falls off exponentially, with an exponent $z(t) < 0$ and a prefactor $A_k(t)$ that varies more slowly than exponentially, i.e.,

$$c_k(t) = A_k(t)\, e^{kz(t)}; \qquad \lim_{k \to \infty} [k^{-1} \log A_k(t)] = 0 \tag{A.28}$$

Depending on the initial conditions, the solutions may have a universal or a transient form. *Universal solutions* have the same form as scaling solutions for large values of the scaling argument r (see below). For $\nu < 1$ one finds that for large cluster sizes

$$A_k(t) \sim a\dot{z}(t)\, k^{-\lambda}; \qquad a^{-1} = \tfrac{1}{2} \int_0^1 dx\, K(x, 1-x)[x(1-x)]^{-\lambda} \tag{A.29}$$

The universal behavior for models with $\nu = 1$ is infinitely more diverse[18] and will not be discussed here. In all cases it follows from (A.28) that $\dot{c}_k \sim k\dot{z}c_k$ as $k \to \infty$. For special initial conditions one finds *transient* solutions, different from (A.29), that cross over to a universal form after an initial period of time. In this paper, therefore, we restrict ourselves to the universal form.

Finally we consider the behavior of the solutions $c_k(t)$ in the scaling limit, where the average cluster size $s(t) \to \infty$ and $k \to \infty$, with the ratio $r = k/s(t)$ fixed. The scaling limit refers to the limit $t \to t_c$ in gelling systems ($\lambda > 1$) and to $t \to \infty$ in nongelling systems. In the scaling limit, the concentrations $c_k(t)$ approach a scale-invariant form, or scaling form[13]:

$$c_k(t) \xrightarrow{S} s(t)^{-\tau'} \varphi(r); \qquad r \equiv k/s(t) \tag{A.30}$$

with $\tau' = 2$ in nongelling systems and $\tau' = \frac{1}{2}(\lambda + 3)$ in gelling systems. Substitution of the Ansatz (A.30) into Smoluchowski's equation gives first an equation for $s(t)$,

$$\dot{s} = ws^{2+\lambda-\tau'} \tag{A.31a}$$

and next a nonlinear integrodifferential equation for the scaling function $\varphi(r)$:

$$\begin{aligned} -w(\tau'\varphi(r) + r\varphi'(r)) &= \lim_{\varepsilon \downarrow 0} \left[\tfrac{1}{2} \int_{\varepsilon r}^{(1-\varepsilon)r} dx\, K(x, r-x)\, \varphi(x)\, \varphi(r-x) \right. \\ &\quad \left. - \varphi(r) \int_{\varepsilon r}^{\infty} dx\, K(r, x)\, \varphi(x) \right] \end{aligned} \tag{A.31b}$$

The constant w in (A.31a), (A.31b) is a separation constant for the r and t dependences. The ε limit in (A.31b) is necessary to exclude possible divergences in the individual integrals on the right-hand side. The form of the scaling functions $\varphi(r)$ for general homogeneous kernels has been studied in Ref. 13. For the details we refer to this work.

APPENDIX B

In this appendix we investigate which models lead to the same simple form (8.12) for the factorial cumulants $e_{mn}(t)$ as was found for the models $K_{ij}=i+j$ and $K_{ij}=ij$. To answer this question, we note first that (8.12) is possible only if the system starts from a *monodisperse* initial distribution. This may be seen from comparison of (8.12) for $t=0$ and the initial condition (4.1) for $e_{mn}(t)$.

To determine which rate constants lead to factorial cumulants of the form (8.12), we substitute the Ansatz (8.12) into Eq. (2.17), with A_{kj} given in (2.11a). One finds that

$$mn\dot{M}_2=\left(n\sum_j jK_{mj}c_j+m\sum_j jK_{nj}c_j\right)M_2-K_{mn}(M_2)^2 \tag{B.1}$$

An equation for $\dot{M}_2$ is found by multiplying Smoluchowski's equation (1.4) with k^2 and summing over all k. The result is

$$\dot{M}_2=\sum_{i,j} ijK_{ij}c_ic_j \tag{B.2}$$

From (B.1) it follows immediately that the rate constants K_{mn} have the form

$$K_{mn}=mB_n+nB_m \tag{B.3}$$

where the constants B_n are defined as

$$B_n\equiv\sum_j jK_{nj}c_j/M_2-\tfrac{1}{2}n\dot{M}_2/(M_2)^2 \tag{B.4}$$

Thus, if e_{mn} has the form (8.12), then necessarily K_{mn} is of the form (B.3). Conversely, for all kernels K_{mn} of the form (B.3), one finds with the use of (B.2) that (B.4) reduces to an identity. We conclude that *all* rate constants of the form (B.3), and *only* such rate constants, lead to (8.12). The only restriction is of course that unphysical rate constants, with $B_n/n\to\infty$ as $n\to\infty$, are excluded. For such kernels pre-gel solutions $c_k(t)$ do not exist, i.e., gelation occurs instantaneously.[25]

Models of the form (B.3) have been called *linear* models by Lushnikov.[5] For such kernels and monodisperse initial conditions,

Lushnikov gives a partial solution of the master equation (1.1). The result has the form (B.1), where $a_k(t)$ can be calculated recursively by quadratures. Similarly, the macroscopic law (1.4) can be solved recursively, as has been shown in Ref. 26.

ACKNOWLEDGMENTS

This Work is part of a research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO). It is a pleasure to thank Matthieu Ernst for his kind and helpful comments on the manuscript. I acknowledge several interesting discussions with Profs. N. G. van Kampen and H. van Beijeren.

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