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Fluctuations in Coagulating Systems

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Time-dependent fluctuations in a system of coagulating particles are studied, using the master equation for the probability distributions $P(\mathbf{m}, t)$ for the occupation numbers $\mathbf{m} = \{m_k\}$ $(k = 1, 2,...)$ of the k-cluster states. Van Kampen's Ω-expansion is used to determine the deterministic (order Ω^0) and fluctuating part (order $\Omega^{-1/2}$) of the solution. We calculate the time-dependent behavior of the fluctuations in the cluster size distribution. The model under consideration is of special interest since it exhibits a phase transition (gelation). For monodisperse initial states we give explicit expressions for the probability distribution of the fluctuations and for the equal-time and two-time correlation functions also near the phase transition. For general initial conditions we study the fluctuations (1) for large cluster sizes, (2) in the scaling limit (near the critical point), and (3) for large times. Our results show that the deterministic approach to coagulation processes (Smoluchowski theory) is invalid very close to the gelpoint t_c and at large times $(t \gtrsim t_M)$, where the distance from the gelpoint and the time t_M depend upon the size of the system.

KEY WORDS: Van Kampen's Ω-expansion; fluctuations in aggregation kinetics; fluctuations near a gelation transition; Smoluchowski's coagulation equation; master equation.

1. INTRODUCTION

Kinetic theory aims at describing the time-dependent behavior of averages and of fluctuations around such averages. There are many different methods for discussing fluctuations in equilibrium and nonequilibrium systems at equal times and at different times, using either methods of statistical mechanics, linear or nonlinear kinetic equations, or the master equation. A general reference is Ref. 1. More references can be found in Ref. 2.

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The structure of the kinetic equations governing the time dependence of these covariances and correlation functions is essentially the same in all methods. The kinetic equation is described by a time-dependent linear kinetic evolution operator, obtained by linearizing the macroscopic evolution equations around the time-dependent average of the fluctuating quantity.

In this paper a general method for describing fluctuations in non-equilibrium systems is applied to a nonlinear kinetic equation describing coagulation processes. It is of particular interest because the coagulation model to be considered undergoes a phase transition (gelation) and the behavior of the fluctuations in the vicinity of this phase transition can be analyzed in all detail.

Two approaches exist to the theoretical treatment of coagulation processes based on mean field ideas, where particles react independent of their mutual distance. On one hand, the deterministic Smoluchoski theory(3,4) provides abundant information about the time evolution of the cluster size distribution for large classes of models, but the fluctuations in the concentrations are neglected. On the other hand, in the stochastic (master equation) approach(5–7) the fluctuations are taken into account, but the method yields only a few exact solutions for special models and special (monodisperse) initial conditions.

We assume that the system is *large*, and we expand the master equation in powers of the inverse system size. This method is known as the Ω-expansion.(1) In this expansion we retain only the first few terms. Thus, we obtain an *approximate* description of the fluctuations, valid for large systems, that is more tractable than the original master equation. We apply the method to one particular model that is of special interest, since it describes the occurrence of a *gelation transition*. Many properties of the fluctuations, including their behavior near the gelpoint, can be calculated exactly.

We discuss the deterministic (Smoluchowski) theory first, and then the master equation approach. In the Smoluchowski theory of coagulation it is assumed that fluctuations in the concentrations are negligibly small. This assumption can only be correct if the volume and the number of particles are *infinitely large*. In this case it suffices to construct a set of macroscopic *rate equations* for the concentrations $c_k(t)$ of clusters of size k ($k = 1, 2, \ldots$). The result is known as Smoluchowski's coagulation equation(8):

$$\dot{c}_k(t) = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i(t)\, c_j(t) - c_k(t) \sum_{j=1}^{\infty} K_{kj} c_j(t) \qquad (k = 1, 2, \ldots) \quad (1.1)$$

Equation (1.1) describes the possible irreversible coagulation reactions between clusters of *finite* size (*sol* particles). If, apart from the clusters of finite size, there occurs also an *infinite* cluster, or *gel*, then Eq. (1.1) has to be supplemented with a term describing reactions between k-mers and the gel.

A different, stochastic approach is needed if the volume V and M, the number of basic units, are *finite*, and the fluctuations are no longer negligible. In this case a state of the system is characterized by the numbers of k-mers $\mathbf{m} = \{m_k\}$, and one considers the probability $P(\mathbf{m}, t)$ that the system is in the state $\mathbf{m}$ at time t. The time evolution of $P(\mathbf{m}, t)$ is then determined by the following *master equation*(3,6,7):

$$\dot{P}(\mathbf{m}, t) = (2V)^{-1} \sum_{i,j \leq M} K_{ij} \Delta_{ij}[m_i(m_j - \delta_{ij}) P(\mathbf{m}, t)] \tag{1.2}$$

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

$$\Delta_{ij} f(\mathbf{m}) = f(\{m_k + \delta_{ik} + \delta_{jk} - \delta_{i+j,k}\}) - f(\mathbf{m}) \tag{1.3}$$

The initial condition for Eq. (1.2) is determined by the initial state $\mathbf{m}(0) \equiv \mathbf{m}_0$, i.e., $P(\mathbf{m}, 0) = 1$ if $\mathbf{m} = \mathbf{m}_0$ and $P(\mathbf{m}, 0) = 0$ otherwise.

The stochastic equations (1.2) and (1.3) have the following interpretation. We distinguish a gain and a loss term, corresponding, respectively, to the first and second terms in the right-hand side of (1.3). The *gain term* shows that the state $\mathbf{m}$ may be reached from any state with an i-mer and a j-mer more and one $(i+j)$-mer less. The transition rates are $V^{-1}K_{ij}(m_i + 1)(m_j + 1)$ if $i \neq j$ and $\frac{1}{2}V^{-1}K_{ii}(m_i + 2)(m_i + 1)$ if $i = j$. The factor V^{-1} expresses the fact that encounters between clusters are less frequent in larger systems. A similar argument shows that the *loss term* in (1.2) represents all possible ways for the system to leave the state $\mathbf{m}$. Everywhere hereafter we set the density equal to unity, i.e., *we choose* $M = V$. This can always be achieved by an appropriate definition of the unit of volume.

The relation between the stochastic model (1.2) with $V = M$ and the deterministic equations (1.1) is that the average number of k-mers per unit volume $\langle m_k(t) \rangle / M$ reduces to $c_k(t)$ in the thermodynamic limit $(M \to \infty)$. Possible complications as a result of gel formation will be discussed below.

An important property of Eq. (1.2), and also of (1.1), is the *conservation of mass*, i.e., of the total number of units in the system. In the master equation approach this conservation law is obvious, since the number of possible states $\mathbf{m}$ is finite, and the mass is conserved in each transition between two states. As a consequence we have

$$\sum_{k=1}^{M} k m_k = M \tag{1.4}$$

Next consider Eq. (1.1). The situation here is more complicated. The reason is that Smoluchowski's equation, for some choices of the rate constants K_{ij}, predicts a *phase transition* at a finite time $t_c > 0$.(9–11) The conservation law takes a different form before and past the gelpoint t_c. In the pre-gel stage ($t < t_c$), all mass is contained in clusters of finite size, i.e.,

$$\sum_{k=1}^{\infty} kc_k(t) = \text{const} = 1 \qquad (t < t_c) \tag{1.5}$$

In the post-gel stage ($t > t_c$) part of the mass is contained in an infinite cluster (gel). Accordingly, the conservation law (1.5) for the sol mass is replaced by

$$\sum_{k=1}^{\infty} kc_k(t) + g(t) = 1 \qquad (t > t_c) \tag{1.6}$$

where $g(t)$ represents the mass of the gel. The constant in the right-hand side of (1.5) and (1.6) is equal to unity, due to our choice $M = V$.

In this paper we consider one particular model, which leads to a phase transition within a finite time. The corresponding rate constants are

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

This choice for the rate constants(12,13) implies that the *reactivity* of a cluster is taken proportional to its *mass*, or volume. For K_{ij} as in (1.7), Smoluchowski's equation (1.1) assumes a particularly simple form. In the pre-gel stage, one finds as a result of the conservation law (1.5)

$$\dot{c}_k(t) = \tfrac{1}{2} \sum_{i+j=k} ijc_i(t)\, c_j(t) - kc_k(t) \tag{1.8}$$

In the post-gel stage, where an infinite cluster is present, Eq. (1.1) does *not* give a correct description of the combined sol–gel system. The reason is that in (1.1) possible sol–gel reactions are not taken into account. Such interactions can be taken into account by adding an extra term to the right-hand side of (1.1), describing the reactivity of the gel. Since we assume that the reactivity of a cluster is proportional to its mass, the extra term to (1.1) is necessarily of the form $-kc_k(t)\, g(t)$. As a consequence of the conservation law (1.6) one finds that $c_k(t)$ satisfies Eq. (1.8) also for $t > t_c$.(9,12)

The macroscopic law (1.8) can be solved exactly for a general initial distribution $c_k(0)$.(14,12) The structure of the solutions has been discussed in detail by Ziff *et al.*(12) In the terminology of Ziff *et al.*, Eq. (1.8) is referred to as the F-model. In order to illustrate the qualitative behavior of the solutions, we give the results for monodisperse initial conditions,(13) i.e., $c_k(0)=\delta_{k1}$:

$$c_k(t)=k^{k-2}(te^{-t})^k/k!\,t \tag{1.9}$$

In the pre-gel stage, i.e., for $t<t_c=1$, $c_k(t)$ falls off exponentially as a function of k. All mass is contained in clusters of finite size, implying that the sol mass is conserved, as in (1.5). At the gelpoint $t_c=1$, the formation of a gel sets in. The sol mass for $t>1$ may readily be calculated from (1.9). One finds that $\sum kc_k(t)=t^*/t$, where t^* is the root of the equation $t^*\exp(-t^*)=t\exp(-t)$ in the interval $0<t^*<1$. The gel mass $g(t)$ is then determined by (1.6). For large times one finds that $g(t)\sim 1-e^{-t}$, implying that eventually all mass is contained in the gel.

Concerning the solutions of the master equation (1.2) with $K_{ij}=ij$, much less is known. The exact solution of the master equation (1.2) is known only in one special case, namely for monodisperse initial conditions, $m_k(0)=M\delta_{k1}$. In this case Eq. (1.2) has in principle been solved by Lushnikov(6) in terms of the generating function of $P(\mathbf{m},t)$. In Appendix A we review and extend Lushnikov's result, and we make a comparison with the results from the Ω-expansion.

For general, nonmonodisperse initial conditions, the solution of Eq. (1.2) is not known. Even in the case of monodisperse initial conditions there still remain interesting properties, such as the two-point correlation functions

$$\langle\!\langle m_i(t_1)\,m_j(t_2)\rangle\!\rangle \equiv \langle [m_i(t_1)-\langle m_i(t_1)\rangle][m_j(t_2)-\langle m_j(t_2)\rangle]\rangle \tag{1.10}$$

which cannot be calculated from the exact solution given in Appendix A. Fortunately, the number of units M involved in coagulation processes such as polymerization is in general very large. For obtaining insight in the stochastic properties of such systems it suffices to calculate approximate results, valid in the limit of a large system ($M\to\infty$).

In this paper we calculate approximate solutions of the master equation, valid if the system is large. Our method is the Ω-expansion developed by van Kampen.(1) It is a systematic expansion of the master equation in powers of the inverse system size. In our case the system size is M.

In the case of Eq. (1.2), the Ω-expansion works as follows. The basic assumption is that for large systems the fluctuations in the number of k-mers $m_k(t)$ are small compared to the average values $\langle m_k\rangle$. More precisely, one assumes that the numbers $m_k(t)$ consist of a macroscopic part $Mc_k(t)$, with $c_k(t)$ given by (1.8), and a fluctuating part $M^{1/2}\xi_k(t)$, i.e.,

$$m_k(t)\equiv Mc_k(t)+M^{1/2}\xi_k(t) \tag{1.11}$$

The idea is that the scale of the new variables $\xi_k(t)$ remains finite[4] as $M \to \infty$. The probability distribution $P(\mathbf{m}, t)$ in (1.2) is then replaced by the probability distribution $\Pi(\boldsymbol{\xi}, t)$ for the fluctuations $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots)$, and Δ_{ij} is written as a differential operator with the use of (1.11). As a result, the master equation (1.2) reduces to a linear Fokker–Planck equation for $\Pi(\boldsymbol{\xi}, t)$ as $M \to \infty$. The Fokker–Planck equation is much more tractable than the original master equation.

This paper is organized as follows. In Section 2 we discuss the expansion of the master equation in powers of M^{-1}. We derive equations for the probability distribution $\Pi(\boldsymbol{\xi}, t)$ and for the averages and covariances of the fluctuations. *Monodisperse initial conditions* are the subject of Section 3. We calculate explicit expressions for the covariances $\langle\langle \xi_l(t)\, \xi_m(t) \rangle\rangle$ and the probability distribution $\Pi(\boldsymbol{\xi}, t)$ and for the two time correlation functions $\langle\langle \xi_l(t_1)\, \xi_m(t_2) \rangle\rangle$. Section 4 is devoted to *general initial conditions.* We give an exact expression for the covariances $\langle\langle \xi_l(t)\, \xi_m(t) \rangle\rangle$ in terms of generating functions, and we study their asymptotic behavior in various limits: for large cluster sizes $(l, m \to \infty)$, in the scaling limit, and in the limit $t \to \infty$. Finally, in Section 5 we summarize and discuss our results. Relevant results from the literature are summarized in Appendices A and B.

2. Ω-EXPANSION OF THE MASTER EQUATION

In gelling systems, the master equation (1.2) is *not* the most appropriate starting point for the Ω-expansion. The reason is that, in order to derive a macroscopic law from (1.2), one has to be able to distinguish between the sol and the gel. In the pre-gel stage there is no problem, since all clusters belong to the sol. In this case the expansion method sketched in the previous section may readily be applied. In the post-gel stage, however, the distinction between sol clusters and the gel is rather vague. The basic problem is that in a finite system such as (1.2) a gel cannot really be defined. In this section we discuss a different expansion method, valid also in the presence of a gel, that does not start from (1.2).

The essential observation is that it is possible, at least in the special model $K_{ij} = ij$, to construct a master equation for the *marginal probability distribution* $P_r(\mathbf{m}^{(r)}, t)$ that, at time t, the numbers of clusters of size $k \leqslant r$ are given by $\mathbf{m}^{(r)} = (m_1, m_2, \ldots, m_r)$. This can be seen by summing Eq. (1.2) over all m_k with $k > r$. It can also be seen as follows. Clusters of size $k \leqslant r$ are involved in *two types of reactions*:

1. They may react among each other. The transition rates for such reactions are the same as in (1.2), but now with $i, j \leqslant r$.

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[4] For monodisperse initial conditions, this may be verified from (A.18), (A.19).

2. k-mers, with $k \leqslant r$, may react with some cluster of size $j > r$. The total transition rate for this process is $M^{-1}km_kG_r$, where $G_r \equiv \sum_{j>r} jm_j$ is the mass contained in clusters larger than r.

In both processes, the transition rates may be expressed as a function of the occupation numbers $\mathbf{m}^{(r)}$ of clusters of size $k \leqslant r$ *only*. For reactions of type 1 this is obvious. For reaction (2) it is a consequence of the conservation law (1.4) for the total number of units, i.e.,

$$G_r = M - \sum_{k=1}^{r} km_k \tag{2.1}$$

As a result, it is possible to construct the following master equation for the marginal probability distribution $P_r(\mathbf{m}^{(r)}, t)$:

$$\begin{aligned} \dot{P}_r(\mathbf{m}^{(r)}, t) = {} & (2M)^{-1} \sum_{i,j \leqslant r} K_{ij} \Delta_{ij}[m_i(m_j - \delta_{ij}) P_r] \\ & + M^{-1} \sum_{i \leqslant r} i\Delta_i[m_i G_r P_r] \end{aligned} \tag{2.2}$$

where Δ_{ij} and Δ_i are difference operators. The operator Δ_{ij} has been given in (1.3). The action of Δ_i is defined for an arbitrary function $f(\mathbf{m})$ as

$$\Delta_i f(\mathbf{m}) = f(\{m_k + \delta_{ik}\}) - f(\mathbf{m}) \tag{2.3}$$

Note that Δ_i works also on the factor G_r, which depends upon $\mathbf{m}^{(r)}$ as a result of (2.1). The master equation (2.2) is a suitable starting point for the Ω-expansion, since (2.2) refers only on *finite* clusters, of size $k \leqslant r$.

The expansion of the master equation (2.2) proceeds as follows. We introduce the concentrations $c_k(t)$ ($k = 1, 2, \dots r$) and the fluctuations $\boldsymbol{\xi}^{(r)} \equiv (\xi_1, \dots, \xi_r)$ as in (1.11), and we write the probability distribution $P_r(\mathbf{m}^{(r)}, t)$ as a function of $\boldsymbol{\xi}^{(r)}$:

$$P_r(\mathbf{m}^{(r)}, t) = M^{-r/2} \Pi_r(\boldsymbol{\xi}^{(r)}, t) \tag{2.4}$$

The factor $M^{-r/2}$ guarantees that Π_r is properly normalized if P_r is normalized. Furthermore, the difference operator Δ_{ij} in (1.3) can be written as a differential operator in terms of the new variables $\boldsymbol{\xi}^{(r)}$:

$$\begin{aligned} \Delta_{ij} &= \exp\left[\sum_{k=1}^{r} (\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \frac{\partial}{\partial m_k}\right] - 1 \\ &= \exp(M^{-1/2} D_{ij}) - 1 \end{aligned} \tag{2.5a}$$

where the operator D_{ij} has been defined as

$$D_{ij}=\sum_{k=1}^{r}(\delta_{ik}+\delta_{jk}-\delta_{i+j,k})\frac{\partial}{\partial\xi_k} \tag{2.5b}$$

In the derivation of (2.5a) and (2.5b) we have used the relation (1.11) between m_k and ξ_k. For large M, Eq. (2.5a) can be expanded in a Taylor series as follows:

$$\Delta_{ij}=M^{-1/2}D_{ij}+\tfrac{1}{2}M^{-1}(D_{ij})^2+\cdots \qquad (M\to\infty) \tag{2.6}$$

The expansion of the operator Δ_i in (2.3) proceeds along similar lines. One finds that

$$\begin{aligned}\Delta_i&=\exp\left(M^{-1/2}\frac{\partial}{\partial\xi_i}\right)-1\\&=M^{-1/2}\frac{\partial}{\partial\xi_i}+\tfrac{1}{2}M^{-1}\frac{\partial^2}{\partial\xi_i^2}+\cdots \qquad (M\to\infty)\end{aligned} \tag{2.7}$$

Next, G_r in (2.1) may be expanded with the use of (1.11) for m_k. For convenience we introduce the notation

$$g_r(t)\equiv 1-\sum_{k=1}^{r}kc_k(t); \qquad \gamma_r(t)\equiv-\sum_{k=1}^{r}k\xi_k(t) \tag{2.8a}$$

so that G_r can be written as

$$G_r(t)=Mg_r(t)+M^{1/2}\gamma_r(t) \tag{2.8b}$$

Clearly, $g_r(t)$ is the fraction of the mass contained in clusters of size $k>r$, and $\gamma_r(t)$ gives the fluctuations in G_r. Finally, we note that the *time derivative* in (2.2) is taken with m_k constant. Constant m_k means, according to (1.11),

$$d\xi_k/dt=-M^{1/2}\dot{c}_k(t) \tag{2.9a}$$

As a consequence we find the following expression for the left-hand side of (2.2):

$$\begin{aligned}\dot{P}_r(\mathbf{m}^{(r)},t)&=M^{-r/2}\left(\frac{\partial\Pi_r}{\partial t}+\sum_{k=1}^{r}\frac{\partial\Pi_r}{\partial\xi_k}\frac{d\xi_k}{dt}\right)\\&=M^{-r/2}\left[\frac{\partial\Pi_r}{\partial t}-M^{1/2}\sum_{k=1}^{r}\dot{c}_k(t)\frac{\partial\Pi_r}{\partial\xi_k}\right]\end{aligned} \tag{2.9b}$$

due to the definition (2.4) of $\Pi_r(\boldsymbol{\xi}^{(r)},t)$.

In order to obtain an equation for the probability distribution $\Pi_r(\xi^{(r)}, t)$, we insert the expressions (1.11) and (2.4)–(2.9) into (2.2). The result is

$$\begin{aligned}
&\frac{\partial \Pi_r}{\partial t} - M^{1/2} \sum_{k=1}^{r} \dot{c}_k(t) \frac{\partial \Pi_r}{\partial \xi_k} \\
&\quad = M^{1/2} \left(\tfrac{1}{2} \sum_{i,j \leqslant r} K_{ij} c_i c_j D_{ij} \Pi_r + \sum_{i \leqslant r} i c_i g_r \frac{\partial \Pi_r}{\partial \xi_i} \right) \\
&\qquad + \left\{ \tfrac{1}{2} \sum_{i,j \leqslant r} K_{ij} [D_{ij}(c_i \xi_j + c_j \xi_i) + \tfrac{1}{2} c_i c_j (D_{ij})^2] \, \Pi_r \right. \\
&\qquad \left. + \sum_{i \leqslant r} i \left[\frac{\partial}{\partial \xi_i} (c_i \gamma_r + g_r \xi_i) + \tfrac{1}{2} c_i g_r \frac{\partial^2}{\partial \xi_i^2} \right] \Pi_r \right\} + O(M^{-1/2}) \qquad (2.10)
\end{aligned}$$

From comparison of the various M orders in (2.10) we first obtain the macroscopic law for $c_k(t)$ and then an equation for $\Pi_r(\xi^{(r)}, t)$.

First we consider the leading terms in (2.10), which are of order $M^{1/2}$. Comparison of the coefficients of $\partial \Pi_r / \partial \xi_k$ yields an equation for the concentrations $c_k(t)$ $(k = 1,..., r)$:

$$\begin{aligned}
\dot{c}_k &= -\tfrac{1}{2} \sum_{i,j \leqslant r} K_{ij} c_i c_j (\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) - k c_k g_r \\
&= \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - k c_k \qquad (k = 1,..., r) \qquad (2.11a)
\end{aligned}$$

An important point is the initial condition for Eq. (2.11a). In this paper we choose the initial value $c_k(0)$ such that the fluctuations ξ_k in (1.11) vanish at $t = 0$, i.e.,

$$c_k(0) \equiv m_k(0)/M; \qquad \xi_k(0) = 0 \qquad (k = 1,..., r) \qquad (2.11b)$$

Since the value of r in (2.11a), (2.11b) is arbitrary, we conclude that Eq. (2.11) holds for *any* finite value of k. Thus, one finds that the macroscopic law corresponding to the master equation (2.2) with $K_{ij} = ij$ is Smoluchowski's coagulation equation in the form (1.8). The relevant results known from the literature concerning the solutions of Eq. (1.8) are summarized in Appendix B.

The next order in (2.10), which are the terms of order M^0, yields an approximate equation for the probability distribution $\Pi_r(\xi^{(r)}, t)$. The approximation is that the terms of order $M^{-1/2}$ in (2.10b) are not taken into account:

$$\frac{\partial \Pi_r}{\partial t} = \tfrac{1}{2} \sum_{i,j \leqslant r} K_{ij}[D_{ij}(c_i\xi_j + c_j\xi_i) + \tfrac{1}{2}c_ic_j(D_{ij})^2]\, \Pi_r + \sum_{i \leqslant r} i \left[\frac{\partial}{\partial \xi_i}(c_i\gamma_r + g_r\xi_i) + \frac{1}{2}\, c_i g_r \frac{\partial^2}{\partial \xi_i^2} \right] \Pi_r \tag{2.12a}$$

The initial condition for (2.12a) is

$$\Pi_r(\xi^{(r)}, 0) = \delta(\xi^{(r)}) \tag{2.12b}$$

This is a result of our choice (2.11b) for $\xi^{(r)}(0)$. Equation (2.12b) guarantees that the probability distribution $\Pi_r(\xi^{(r)}, t)$ is properly normalized.

Equation (2.12a) is a linear, second-order partial differential equation in the variables $\xi^{(r)}$ and t. More precisely, Eq. (2.12a) has the form of a multivariate linear Fokker–Planck equation,$^{(15)}$ i.e.,

$$\frac{\partial \Pi_r}{\partial t} = -\sum_{k,j \leqslant r} A_{kj}(t) \frac{\partial}{\partial \xi_k}(\xi_j \Pi_r) + \frac{1}{2} \sum_{k,l \leqslant r} B_{kl}(t) \frac{\partial^2 \Pi_r}{\partial \xi_k\, \partial \xi_l} \tag{2.13}$$

where the matrices A_{kj} and B_{kl} depend explicitly upon time. To see this, we insert into (2.12a) the explicit forms of D_{ij} in (2.5b) and of γ_r in (2.8a), which depends explicitly on ξ_i $(i = 1,..., r)$. Moreover, we replace the factor $(c_i\xi_j + c_j\xi_i)$ by $2c_i\xi_j$, which is allowed on account of the symmetry with respect to i and j. As the result, we find an equation of the form (2.13), where the matrices A_{kj} and B_{kl} are given, respectively, by

$$\begin{aligned} A_{kj}(t) &= -\sum_{i \leqslant r} K_{ij}c_i(\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) + kjc_k - kg_r\delta_{kj} \\ &= -k\delta_{kj} + j(k-j)\, c_{k-j}(t) \end{aligned} \tag{2.14a}$$

and

$$\begin{aligned} B_{kl}(t) &= \tfrac{1}{2} \sum_{i,j \leqslant r} K_{ij}c_ic_j(\delta_{ik} + \delta_{jk} - \delta_{i+j,k})(\delta_{il} + \delta_{jl} - \delta_{i+j,l}) + kc_k\, g_r\delta_{kl} \\ &= \delta_{kl} \left[kc_k(t) + \tfrac{1}{2} \sum_{i+j=k} ijc_ic_j \right] + klc_kc_l \\ &\quad - [k(l-k)\, c_kc_{l-k} + l(k-l)\, c_lc_{k-l}] \end{aligned} \tag{2.14b}$$

In (2.14a), (2.14b) it is understood that $c_j(t) \equiv 0$ if $j \leqslant 0$.

The Fokker–Planck equation (2.13) for $\Pi_r(\xi^{(r)}, t)$ can be solved *exactly* in terms of the averages $\langle \xi_m \rangle$ and the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ of the fluctuations, which are defined, respectively, as

$$\langle \xi_m(t) \rangle \equiv \int d\xi^{(r)}\, \xi_m \Pi_r(\xi^{(r)}, t) \qquad (m \leqslant r) \tag{2.15a}$$

and

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle \equiv \langle \xi_m(t)\, \xi_n(t) \rangle - \langle \xi_m(t) \rangle \langle \xi_n(t) \rangle \qquad (m, n \leqslant r) \tag{2.15b}$$

More precisely, it can be shown (Ref. 1, Section VIII.6) that the solution of Eq. (2.13) with the initial condition (2.12b) is the multivariate Gaussian distribution determined by the averages and covariances (2.15a), (2.15b). If we define the covariance matrix $\Xi(t)$ as

$$\Xi_{mn}(t) \equiv \langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle \qquad (m, n \leqslant r) \tag{2.16}$$

then $\Pi_r(\xi^{(r)}, t)$ may be expressed in terms of $\langle \xi^{(r)} \rangle$ and Ξ as follows:

$$\Pi_r(\xi^{(r)}, t) = (2\pi)^{-r/2} (\mathrm{Det}\, \Xi)^{-1/2} \times \exp[-\tfrac{1}{2}(\xi^{(r)} - \langle \xi^{(r)} \rangle) \cdot \Xi^{-1} \cdot (\xi^{(r)} - \langle \xi^{(r)} \rangle)] \tag{2.17}$$

Thus, in principle, $\Pi_r(\xi^{(r)}, t)$ is known if the covariances $\langle\langle \xi_m \xi_m \rangle\rangle$ and the averages $\langle \xi_m \rangle$ have been calculated.

First we consider the average fluctuations $\langle \xi_m(t) \rangle$ in (2.15a). In order to obtain an equation for $\langle \xi_m \rangle$, we multiply (2.13) with ξ_m and integrate over all $\xi^{(r)}$. Partial integration over ξ_k and ξ_l shows that the *second* term on the right in (2.13) does not contribute. The *first* term yields a contribution only if $k = m$, and we find

$$\frac{d}{dt} \langle \xi_m \rangle = \sum_{j \leqslant r} A_{mj}(t) \langle \xi_j \rangle \qquad (m = 1,..., r) \tag{2.18}$$

The initial condition for (2.18) follows from (2.11b) as $\langle \xi_m(0) \rangle = 0$ $(m = 1,..., r)$. Since (2.18) is a linear equation of $\langle \xi^{(r)} \rangle$, we find that the average fluctuations vanish for all $t \geqslant 0$:

$$\langle \xi_m(t) \rangle = 0 \qquad (\text{all } t \geqslant 0; \quad m = 1,..., r) \tag{2.19}$$

Since the value of r in (2.19) is arbitrary, we infer that $\langle \xi_m(t) \rangle = 0$ for *all finite values of m.*

Similarly, we obtain an equation for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$, which are defined in (2.15b). Note that in our case the covariances are *equal* to the second moment $\langle \xi_m(t)\, \xi_n(t) \rangle$ as a result of (2.19). Multiplication of (2.13) with $\xi_m \xi_n$ and integration over all $\boldsymbol{\xi}^{(r)}$ yields the following equation for $\langle\langle \xi_m \xi_n \rangle\rangle$, to be solved with the initial condition $\langle\langle \xi_m(0)\, \xi_n(0) \rangle\rangle = 0$:

$$\frac{d}{dt} \langle\langle \xi_m \xi_n \rangle\rangle = \sum_j \left(A_{nj} \langle\langle \xi_m \xi_j \rangle\rangle + A_{mj} \langle\langle \xi_n \xi_j \rangle\rangle \right) + B_{mn} \tag{2.20}$$

In the derivation of (2.20), we assumed that $m \leqslant r$ and $n \leqslant r$. However, since the value of r is arbitrary, one finds that Eq. (2.20) holds for *all finite values of m and n.* The matrix elements A_{kj} and B_{kl} have been given in (2.14a), (2.14b). Note that A_{kj} and B_{kl} are independent of r.

For future use we note that a drastic simplification of Eq. (2.20) occurs if we transform from $\langle\langle \xi_m \xi_n \rangle\rangle$ to a new variable $e_{mn}(t)$ defined as

$$e_{mn}(t) \equiv \langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle - \delta_{mn} c_n(t) \tag{2.21}$$

In order to obtain an expression for $e_{mn}(t)$, we substitute the definition (2.21) into (2.20). The result is

$$\dot{e}_{mn} = \sum_j \left(A_{nj} e_{mj} + A_{mj} e_{nj} \right) + B_{mn} + A_{nm} c_m + A_{mn} c_n - \delta_{mn} \dot{c}_n \tag{2.22}$$

Insertion into (2.22) of the explicit expressions (2.14a), (2.14b) for A_{mn} and B_{mn}, in combination with the macroscopic law (2.11a), yields the following equation for $e_{mn}(t)$:

$$\dot{e}_{mn} = \sum_j \left(A_{nj} e_{mj} + A_{mj} e_{nj} \right) + mnc_m c_n \tag{2.23a}$$

$$= -(m+n) e_{mn} + \sum_{i+j=n} ijc_i e_{mj} + \sum_{i+j=m} ijc_i e_{nj} + mnc_m c_n \tag{2.23b}$$

The initial condition for Eq. (2.23) is $e_{mn}(0) = -\delta_{mn} c_n(0)$. The simplification in (2.23) becomes particularly clear if one compares Eq. (2.23a) with the equation (2.20) for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$. Both equations are linear and inhomogeneous, but the inhomogeneity in (2.23a) is much simpler than in (2.20). The solution of Eq. (2.23) for monodisperse initial conditions will be given in Section 3. The solution for general initial conditions $c_k(0)$ is the subject of Section 4.

We add a few remarks. The first concerns the *pre-gel stage* $(t < t_c)$, where the sol mass is conserved. In this case the conservation law (1.4), in combination with (1.5) and (1.11), implies the following relation for the fluctuations $\boldsymbol{\xi} = (\xi_1, \xi_2, \ldots)$:

$$\sum_{k=1}^{\infty} k \xi_k = 0 \qquad (t < t_c) \tag{2.24}$$

The property (2.24) may also be verified explicitly in the Fokker–Planck equation (2.13) with $r \to \infty$ or, equivalently, in Eq. (2.20). To see this, we introduce

$$X(t) \equiv \left\langle \left(\sum_{k=1}^{\infty} k\xi_k \right)^2 \right\rangle = \sum_{m,n} mn \langle \xi_m(t)\, \xi_n(t) \rangle \tag{2.25}$$

An equation for $X(t)$ can be obtained from (2.20) by multiplying (2.20) with mn and summing over all m and n. The result is

$$\frac{d}{dt} X(t) = 2 \sum_{m,n,j} mnA_{nj} \langle\!\langle \xi_m \xi_j \rangle\!\rangle + \sum_{m,n} mnB_{mn} \tag{2.26}$$

In the pre-gel stage, where (1.5) holds, the sum involving B_{mn} vanishes. This may be seen from the explicit expression (2.14b) for B_{mn}. Similarly, it follows from (2.14a) that for $t < t_c$, $\sum_n nA_{nj} = jM_2(t)$, where the second moment $M_2(t) = \sum k^2 c_k(t)$ has been defined in (B.5). As a result, Eq. (2.26) takes the form of a closed differential equation for $X(t)$:

$$\frac{d}{dt} X(t) = 2M_2(t)\, X(t) \qquad (t < t_c) \tag{2.27}$$

to be solved with the initial condition $X(0) = 0$. The solution is $X(t) = 0$ for all $t < t_c$. Hence, (2.24) has been proved using the Fokker–Planck equation (2.13).

Our second and final remark is concerned with the post-gel stage and, more specifically, with the *definition of a gel.* The number of units in the gel, which is denoted as $G(t)$, may be determined from (2.8a), (2.8b) if we take the limit $r \to \infty$. The result is

$$G(t) = Mg(t) + M^{1/2}\gamma(t) \tag{2.28a}$$

where we have defined

$$g(t) = 1 - \sum_{k=1}^{\infty} kc_k(t); \qquad \gamma(t) = -\sum_{k=1}^{\infty} k\xi_k(t) \tag{2.28b}$$

Clearly $g(t)$ represents the average gel fraction and $\gamma(t)$ gives the fluctuations in the gel. The point is that the equations (2.28a), (2.28b) for the gel are meaningful *only* within the context of the Ω-expansion, i.e., in the limit $M \to \infty$. This clarifies our remark at the beginning of this section, that the gel cannot really be defined in a finite system. For instance, the gel could not be defined by taking the limit $r \to \infty$ in Eq. (2.1), i.e., before the Ω-expansion is applied.

3. MONODISPERSE INITIAL CONDITIONS

In this section we consider the special case of an initially monodisperse system, i.e.,

$$m_k(0) = M\delta_{k1}; \qquad c_k(0) = \delta_{k1} \tag{3.1}$$

The case of monodisperse initial conditions is relatively easy, and many properties of the fluctuations may be calculated explicitly. This section is subdivided into three parts. In Section 3.1 we calculate the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$, and we discuss their properties in the pre- and post-gel stages. The results will be used in Section 3.2 to obtain the marginal probability density $\Pi_r(\xi^{(r)}, t)$ for an arbitrary value of r. Finally, in Section 3.3 we calculate the correlation functions $\langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle$.

3.1. The Covariances

The covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ can be calculated from (2.20) or, equivalently, from Eq. (2.23) for $e_{mn}(t)$. In Section 4.1 we use generating function techniques to solve Eq. (2.23) and we find that $e_{mn}(t)$ has a remarkably simple form if the initial distribution is monodisperse, namely

$$e_{mn}(t) = -(1-t)\, mnc_m(t)\, c_n(t) \tag{3.2}$$

Here we verify simply by substitution of (3.2) into (2.23) that Eq. (3.2) gives the correct expression for $e_{mn}(t)$ and satisfies the correct initial condition. In verifying (3.2) it is convenient to use the following relation:

$$\begin{aligned} \sum_{i+j=n} ijc_i e_{mj} &= -(1-t)\, mc_m \sum_{i+j=n} ij^2 c_i c_j \\ &= -(1-t)\, mnc_m \cdot \tfrac{1}{2} \sum_{i+j=n} ijc_i c_j \\ &= -(1-t)\, mnc_m(\dot{c}_n + nc_n) \end{aligned} \tag{3.3}$$

In the derivation of (3.3) we have used Smoluchowski's equation (1.8).

As an immediate consequence of Eq. (3.2) and the definition (2.21) of $e_{mn}(t)$, we find the following result for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$:

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle = \delta_{mn} c_n(t) - (1-t)\, mnc_m(t)\, c_n(t) \tag{3.4}$$

in agreement with Lushnikov's exact solution, i.e., Eq. (A.19). Equation (3.4) has the following interpretation. First we consider the case $m \neq n$. In the pre-gel stage ($t < 1$) one finds that $\langle\langle \xi_m \xi_n \rangle\rangle$ is *negative*. This implies simply that if the number of m-mers exceeds the average ($\xi_m > 0$), there will, on the average, be fewer n-mers ($\xi_n < 0$). In the post-gel stage ($t > 1$) it follows from (3.4) that the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ are *positive*. In this case (3.4) gives the surprising prediction that if $\xi_m > 0$, then most likely the mass of the sol phase as a whole exceeds the average, so that there is less gel (and vice versa for fluctuations $\xi_m < 0$). Finally, if m and n in (3.4) are equal, we observe that the variances

$$\langle\langle (\xi_m(t))^2 \rangle\rangle = c_m(t)[1 - (1-t)\, m^2 c_m(t)] \tag{3.5}$$

are strictly positive for all $t > 0$. In the post-gel stage ($t > 1$) this is obvious. In the pre-gel stage it is a consequence of the inequality $m^2 c_m(t) < M_2(t) = (1-t)^{-1}$, where we used Eq. (B.11) for the second moment $M_2(t)$.

The result (3.4) for the covariances in the sol may be used to calculate the covariances of the fluctuations in the sol and the gel. From (3.4) and the definition (2.28b) of the fluctuation $\gamma(t)$ in the mass of the gel it follows that

$$\begin{aligned}\langle\langle \xi_m(t)\, \gamma(t) \rangle\rangle &= -\sum_{n=1}^{\infty} n \langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle \\ &= -m c_m(t)[1 + (t-1)\, M_2(t)]\end{aligned} \tag{3.6}$$

We note that the right-hand side of (3.6) vanishes in the pre-gel stage, where $M_2(t) = (1-t)^{-1}$. Physically this is obvious, since for $t < 1$ there is no gel. This may also be seen from the conservation law (2.24), which implies $\gamma(t) = 0$ if $t < 1$. The variance of the gel fluctuations $\gamma(t)$ can readily be determined from (3.6) by multiplying with $-m$ and summing over all m. The result is

$$\langle\langle (\gamma(t))^2 \rangle\rangle = M_2(t)[1 + (t-1)\, M_2(t)] \tag{3.7}$$

where $M_2(t) = (1-t)^{-1}$ if $t < 1$, and $M_2(t) \sim (t-1)^{-1}$ if $t \downarrow 1$, as may be seen from (B.11) and (B.12). Finally, we remark that the *average* fluctuation in the gel mass vanishes for all $t > 0$:

$$\langle \gamma(t) \rangle = -\sum_m m \langle \xi_m(t) \rangle = 0 \tag{3.8}$$

This follows directly from Eq. (2.19).

3.2. The Probability Distribution

The next step is to calculate the marginal probability distribution $\Pi_r(\boldsymbol{\xi}^{(r)}, t)$ in (2.17), which is completely determined by the average fluctuations $\langle \boldsymbol{\xi}^{(r)} \rangle$ and the covariance matrix $\Xi(t)$. The averages $\langle \boldsymbol{\xi}^{(r)} \rangle$ vanish for all $t \geqslant 0$ as a result of (2.19). Furthermore, it follows from the definition (2.16), in combination with (3.4), that the matrix elements Ξ_{mn} are equal to

$$\Xi_{mn}(t) = \delta_{mn} c_n(t) - (1-t)\, mnc_m(t)\, c_n(t) \qquad (m, n \leqslant r) \tag{3.9}$$

In order to obtain an explicit expression for $\Pi_r(\xi^{(r)}, t)$, we calculate the inverse of $\Xi(t)$ first and then its determinant.

The inverse of the matrix Ξ in (3.9) has a particularly simple form,

$$(\Xi^{-1})_{nj} = (1/c_n)\delta_{nj} + nj/v_r \qquad (n, j \leqslant r) \tag{3.10a}$$

where the time dependence of v_r is given for all $t \geqslant 0$ by

$$v_r(t) = (1-t)^{-1} - \sum_{k=1}^{r} k^2 c_k(t) \tag{3.10b}$$

It can readily be verified by matrix multiplication of (3.9) and (3.10a) that Ξ^{-1} in (3.10) is indeed the inverse of Ξ in (3.9).

The calculation of the determinant of Ξ is less trivial. The simplest way to obtain the prefactor of the exponential in (2.17) is as follows. In order to simplify the expressions for $\Pi_r(\xi^{(r)}, t)$, we introduce the one-dimensional Gaussian distribution with zero mean and variance σ^2, which is defined as

$$g(x; \sigma^2) \equiv (2\pi\sigma^2)^{-1/2} \exp(-x^2/2\sigma^2) \tag{3.11}$$

With the use of (3.11) and the explicit expression (3.10) for Ξ^{-1}, we can write Eq. (2.17) in the form

$$\Pi_r(\xi^{(r)}, t) = (2\pi)^{-r/2} (\det \Xi)^{-1/2} \exp\left[-\sum_{j=1}^{r} \xi_j^2/2c_j - \left(\sum_{j=1}^{r} j\xi_j\right)^2 \Big/ 2v_r \right] \tag{3.12a}$$

$$= C(t)\, g\left(\sum_{j=1}^{r} j\xi_j; v_r\right) \prod_{j=1}^{r} g(\xi_j; c_j) \tag{3.12b}$$

where $C(t)$ is an as yet unknown normalization factor.

In order to calculate $C(t)$ in (3.12b), we integrate Eq. (3.12) over all $\xi^{(r)}$. Since we assume that the probability distribution $\Pi_r(\xi^{(r)}, t)$ is properly normalized, this yields

$$\begin{aligned} 1 &= C(t) \int d\boldsymbol{\eta}^{(r)}\, g\left(\sum_{j=1}^{r} \eta_j; v_r\right) \prod_{j=1}^{r} g(\eta_j; j^2 c_j) \\ &= C(t) \int_{-\infty}^{\infty} dx\, g(x; v_r) \int d\boldsymbol{\eta}^{(r)}\, \delta\left(\sum_{j=1}^{r} \eta_j - x\right) \prod_{j=1}^{r} g(\eta_j; j^2 c_j) \end{aligned} \tag{3.13}$$

In the first step in (3.13) we have introduced new variables $\boldsymbol{\eta}^{(r)}=(\eta_1,..., \eta_r)$, which are related to $\boldsymbol{\xi}^{(r)}$ as $\eta_j \equiv j\xi_j$. In the second step we introduced an additional delta-function. The reason for this is that the second integral on the right in (3.13) is by definition (Ref. 1, Section I.5) the probability density that the variable $\sum_{j=1}^{r} \eta_j$ assumes values in the interval $(x, x+dx)$. For Gaussian variables η_j with variance j^2c_j we know (Ref. 1, Section I.6) that $\sum_{j=1}^{r} \eta_j$ is again normally distributed, now with variance $\sum_{j=1}^{r} j^2c_j$. Thus, Eq. (3.13) reduces to

$$1 = C(t) \int_{-\infty}^{\infty} dx\, g(x; v_r)\, g\left(x; \sum_{j=1}^{r} j^2c_j\right) \tag{3.14}$$

Calculation of the integral in (3.14) is elementary. As a result we find that

$$C(t) = [2\pi/(1-t)]^{1/2} \tag{3.15a}$$

where we have used the explicit form (3.10b) of $v_r(t)$. As an immediate consequence we find for the factor $\det \Xi$ in (3.12a)

$$\det \Xi = (1-t) v_r \prod_{j=1}^{r} c_j \tag{3.15b}$$

Note that $\det \Xi$ is strictly positive for all $t > 0$. For $t > 1$ this is obvious from (3.10b), since in this case $v_r(t) < 0$. For $t < 1$ the positivity of $\det \Xi$ or $v_r(t)$ follows from (B.11) with $t_c = 1$.

One finds the following explicit expressions for $\Pi_r(\boldsymbol{\xi}^{(r)}, t)$. In the pre-gel stage $(t < 1)$, where v_r is *positive*, it follows from (3.12b) that

$$\Pi_r(\boldsymbol{\xi}^{(r)}, t) = \left(\frac{2\pi}{1-t}\right)^{1/2} g\left(\sum_{j=1}^{r} j\xi_j; v_r\right) \prod_{j=1}^{r} g(\xi_j; c_j) \qquad (t<1) \tag{3.16a}$$

The same expression (3.16a) is valid in the post-gel stage, but in this case v_r is *negative*. An alternative form for $t > 1$ is obtained with the use of (3.11), namely

$$\Pi_r(\boldsymbol{\xi}^{(r)}, t) = [(t-1)\,|v_r|]^{-1/2} \exp\left[\left(\sum_{j=1}^{r} j\xi_j\right)^2 \Big/ 2\,|v_r|\right] \prod_{j=1}^{r} g(\xi_j; c_j) \qquad (t>1) \tag{3.16b}$$

Note that, for large ξ_j, the exponential in (3.16b) becomes *large*. Also note that the normalizability of Π_r is guaranteed by the factor $g(\xi_j; c_j)$, which has a smaller variance.

Finally, we discuss the probability distribution in the limit $r \to \infty$. The result is dramatically different in the pre- and post-gel stages. For $t < 1$ we know from (3.10b) and (B.11) that $v_r \to 0$ as $r \to \infty$. As a result, the factor $g(\sum j\xi_j; v_r)$ in (3.16a) reduces to a delta function:

$$\Pi(\xi, t) = \left(\frac{2\pi}{1-t}\right)^{1/2} \delta\left(\sum_{j=1}^{\infty} j\xi_j\right) \prod_{j=1}^{\infty} g(\xi_j; c_j) \qquad (t<1) \tag{3.17}$$

On the other hand, in the post-gel stage, where

$$|v_r| \to v_\infty \equiv (t-1)^{-1} + M_2(t) \qquad (r \to \infty) \tag{3.18}$$

we infer from (3.16a), (3.16b) that, as $r \to \infty$, Π_r takes the form

$$\Pi(\xi, t) = \left(\frac{2\pi}{t-1}\right)^{1/2} g(i\gamma; v_\infty) \prod_{j=1}^{\infty} g(\xi_j; c_j) \tag{3.19a}$$

$$= [(t-1)v_\infty]^{-1/2} \exp(\gamma^2/2v_\infty) \prod_{j=1}^{\infty} g(\xi_j; c_j) \qquad (t>1) \tag{3.19b}$$

where $i = \sqrt{-1}$, and γ has been defined in (2.28b). The delta function in (3.17) clearly reflects the conservation law (2.24), which holds only in the pre-gel stage. At the gelpoint t_c the delta peak changes abruptly to a Gaussian form with an *imaginary* variable and an *infinite* variance. For $t>1$ the variance $v_\infty(t)$ decreases monotonically, and vanishes as $t \to \infty$. This reflects the behavior (3.7) of the fluctuations in the gel: the size of the fluctuations diverges as $t \downarrow t_c$, and vanishes in the limit $t \to \infty$, when all mass is contained in the gel.

3.3. The Correlation Functions

In this subsection we calculate the (two-time) correlation functions $\kappa_{nm}(t_2, t_1)$, which are defined as

$$\begin{aligned}\kappa_{nm}(t_2, t_1) &\equiv \langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle \\ &= \langle \xi_m(t_1)\, \xi_n(t_2) \rangle - \langle \xi_m(t_1) \rangle \langle \xi_n(t_2) \rangle\end{aligned} \tag{3.20}$$

We assume that $t_2 \geqslant t_1 \geqslant 0$. From Section 2, Eq. (2.19), we know that the average fluctuations $\langle \xi_m(t_1) \rangle$ and $\langle \xi_n(t_2) \rangle$ vanish for all t_1 and t_2. Hence $\kappa_{nm}(t_2, t_1)$ is also given by

$$\kappa_{nm}(t_2, t_1) = \langle \xi_m(t_1)\, \xi_n(t_2) \rangle \qquad (0 \leqslant t_1 \leqslant t_2) \tag{3.21}$$

The method for calculating $\kappa_{nm}(t_2, t_1)$ consists of two steps. In the first step we assume that at t_1 the fluctuations are given by $\xi(t_1)$, and we calculate the conditional average $\langle \xi_n(t_2) | \xi(t_1) \rangle$ of ξ_n at time t_2. In the second step we multiply $\langle \xi_n(t_2) | \boldsymbol{\xi}(t_1) \rangle$ with $\xi_m(t_1)$ and we average over all possible values of $\boldsymbol{\xi}(t_1)$. The result is (3.21). From now onward we drop the label $\boldsymbol{\xi}(t_1)$, and we denote the conditional averages $\langle \xi_n(t_2) | \boldsymbol{\xi}(t_1) \rangle$ simply by $\overline{\xi_n(t_2)}$.

As a *first step* we calculate the conditional averages $\overline{\xi_n(t_2)}$ for a given initial value $\boldsymbol{\xi}(t_1)$. The averages $\overline{\xi_n(t)}$ satisfy the relation (2.18), with A_{mj} given in (2.14a), i.e.,

$$\frac{d}{dt}\overline{\xi_n} = \sum_{i+j=n} ijc_i\overline{\xi_j} - n\overline{\xi_n} \tag{3.22}$$

In order to solve (3.22), we introduce the generating function $\chi(x, t)$ of $\overline{\xi_n(t)}$, which is defined as

$$\chi(x, t) \equiv \sum_{n=1}^{\infty} \overline{\xi_n(t)}\, e^{nx} \tag{3.23}$$

An equation for $\chi(x, t)$ can be obtained from (3.22) by multiplication with e^{nx} and summation over all n. The result is

$$\frac{\partial \chi}{\partial t} + [1 - f(x, t)] \frac{\partial \chi}{\partial x} = 0 \tag{3.24}$$

where $f(x, t)$ is the generating function of $kc_k(t)$ satisfying (B.3).

Equation (3.24) can be solved as follows. We transform from $\chi(x, t)$ to a new function $W(z, t)$, which is defined as

$$W(z, t) \equiv \chi(x, t); \qquad z \equiv f(x, t) \tag{3.25}$$

where $z = f(x, t)$ is the image of x at time t. To obtain the initial condition $W(z, t)$ at t_1 from a given function $\chi(x, t_1)$, we need the point x_1 that is mapped at time t_1 onto the same $z = f(x_1, t_1)$. Hence

$$W(z, t_1) = W(f(x_1, t_1), t_1) = \chi(x_1, t_1) \tag{3.26}$$

Insertion of the definition (3.25) of $W(z, t)$ into (3.24) and use of the differential equation (B.3) for $f(x, t)$ shows that $W(z, t)$ is independent of t, i.e.,

$$\frac{\partial}{\partial t} W(z, t) = 0 \tag{3.27}$$

From (3.27) we infer that $\chi(x, t)$ may be expressed in terms of its initial value $\chi(x, t_1)$ as follows:

$$\chi(x, t) = W(z, t) = W(z, t_1) = \chi(x_1, t_1) \tag{3.28}$$

The relation between the points (x, t) and (x_1, t_1) having the same image z, i.e.,

$$f(x, t) = z = f(x_1, t_1) \tag{3.29a}$$

is given by

$$x_1 = x + (t - t_1)[f(x, t) - 1] \tag{3.29b}$$

This can be seen from (B.5a), (B.5b).

The conditional average $\overline{\xi_n(t_2)}$ can now be obtained as the coefficient of e^{nx} in $\chi(x, t_2)$. If we introduce the notation $y \equiv e^x$, then $\overline{\xi_n(t_2)}$ can be written as a contour integral in the complex plane as follows:

$$\overline{\xi_n(t_2)} = \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \chi(x, t_2) \tag{3.30}$$

The path of integration in (3.30) is a closed contour in the complex y plane, which circles the origin once in the counterclockwise direction. Insertion of (3.28) into (3.30) and use of the definition (3.23) of $\chi(x, t)$ gives

$$\begin{aligned} \overline{\xi_n(t_2)} &= \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} \chi(x_1, t_1) \\ &= \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)\, \xi_l(t_1) \end{aligned} \tag{3.31a}$$

where $Y_{nl}(t_2, t_1)$ is defined as

$$Y_{nl}(t_2, t_1) \equiv \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} e^{lx_1} \tag{3.31b}$$

The matrix $Y(t_2, t_1)$, usually called the *evolution matrix* of the problem (3.22), relates the average fluctuations $\overline{\xi_n(t_2)}$ at time t_2 to the initial value $\xi(t_1)$.

The last part of step one is to calculate the explicit time dependence of the matrix Y_{nl} in (3.31b). In order to do this, we express x and x_1 in terms of z, t_2, and t_1 with the use of (3.29a) and (B.32). (Note that in this stage for the first time we use the condition that initially the system is monodisperse.) The result is

$$y = e^x = ze^{t_2(1-z)}; \qquad e^{x_1} = ze^{t_1(1-z)} \tag{3.32}$$

Insertion of (3.32) into (3.31b) gives, after some algebra

$$Y_{nl}(t_2, t_1) = e^{lt_1 - nt_2} \frac{1}{2\pi i} \oint \frac{dz}{z^{n-l+1}} [(1 - t_2 z)\, e^{(nt_2 - lt_1)z}] \tag{3.33}$$

The contour integral in (3.33) is equal to the coefficient of z^{n-l} in the factor $[\cdots]$. Expansion of the exponential $e^{(nt_2-lt_1)z}$ in $[\cdots]$ readily yields the following explicit expression for $Y_{nl}(t_2, t_1)$:

$$Y_{nl}(t_2, t_1) = l(t_2 - t_1) \frac{(nt_2 - lt_1)^{n-l-1}}{(n-l)!} e^{lt_1 - nt_2} \tag{3.34}$$

We note that Y_{nl} vanishes if $l > n$. Combination of (3.34) and (3.31a) finally gives the desired expression for the conditional average $\overline{\xi_n(t_2)}$.

The *second step* in the calculation of $\kappa_{nm}(t_2, t_1)$ is to multiply (3.31a) with $\xi_m(t_1)$ and to average over all possible values of $\xi(t_1)$. In combination with (3.21) and (3.4) we find that

$$\kappa_{nm}(t_2, t_1) = \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1) \langle\langle \xi_l(t_1)\, \xi_m(t_1) \rangle\rangle \tag{3.35a}$$

$$= Y_{nm}(t_2, t_1)\, c_m(t_1) - (1 - t_1)\, mc_m(t_1) \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)\, lc_l(t_1) \tag{3.35b}$$

The second term in (3.35b) may be simplified with the use of (3.31b), namely

$$\begin{aligned} \sum_{l=1}^{\infty} Y_{nl}(t_2, t_1)\, lc_l(t_1) &= \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} f(x_1, t_1) \\ &= \frac{1}{2\pi i} \oint \frac{dy}{y^{n+1}} f(x, t_2) \\ &= nc_n(t_2) \end{aligned} \tag{3.36}$$

In the second and third lines of (3.36) we have used, respectively, Eq. (B.5a) and the definition (B.2) of $f(x, t)$. Combination of (3.35b) and (3.36) yields

$$\kappa_{nm}(t_2, t_1) = Y_{nm}(t_2, t_1)\, c_m(t_1) - (1 - t_1)\, mnc_m(t_1)\, c_n(t_2) \tag{3.37}$$

In combination with (3.34) this gives the desired explicit form of the correlation functions $\kappa_{nm}(t_2, t_1)$. As a special case we consider the autocorrelation functions $\langle\langle \xi_m(t_1)\, \xi_m(t_2) \rangle\rangle$, which are obtained from (3.37) if we set $n = m$. The result is

$$\kappa_{mm}(t_2, t_1) = c_m(t_1)\, e^{-m(t_2 - t_1)} - (1 - t_1)\, m^2 c_m(t_1)\, c_m(t_2) \tag{3.38}$$

One readily verifies that, in the limit $t_2 \downarrow t_1$, Eqs. (3.37) and (3.38) reduce to the results (3.4) and (3.5) for the covariances $\langle\langle \xi_m(t_1)\, \xi_n(t_1) \rangle\rangle$. The long-time behavior of the nonequilibrium autocorrelation function (3.38), with $t_2 \gg t_1$, is determined by the long-time behavior of $c_m(t_2)$ given in (B.31). The relative magnitude of the second term as compared to the first one in (3.38) grows as t_2^{m-1} and becomes positive (negative) for sufficiently large t_2 if the initial time t_1 occurs after (before) the gel point.

Finally, we discuss the differences between the pre- and post-gel stages. We consider the *pre-gel stage* first. In this case the mass conservation law (2.24), i.e., $\sum k\xi_k = 0$, implies the following relations for the correlation functions $\kappa_{nm}(t_2, t_1)$:

$$\sum_{m=1}^{\infty} m\kappa_{nm}(t_2, t_1) = 0 \qquad (t_1 < 1) \tag{3.39a}$$

$$\sum_{n=1}^{\infty} n\kappa_{nm}(t_2, t_1) = 0 \qquad (t_1 \leqslant t_2 < 1) \tag{3.39b}$$

In view of (3.21) this is obvious, since $\sum_m m\xi_m(t_1) = 0$ and $\sum_n n\xi_n(t_2) = 0$. The relations (3.39a), (3.39b) also may be verified from the explicit expression (3.37) for $\kappa_{nm}(t_2, t_1)$.

Next we consider the correlation functions in the *post-gel stage*, where $t_2 > 1$, and possibly also $t_1 > 1$. The correlation functions (3.37) in the sol, in combination with the definition (2.28b) of $\gamma(t)$, also determine the correlation functions of the gel. The *cross-correlations* between the sol and the gel are given by

$$\kappa_{nG}(t_2, t_1) \equiv \langle\!\langle \gamma(t_1)\, \xi_n(t_2) \rangle\!\rangle = -\sum_{m=1}^{\infty} m\kappa_{nm}(t_2, t_1) \tag{3.40a}$$

$$\kappa_{Gm}(t_2, t_1) \equiv \langle\!\langle \xi_m(t_1)\, \gamma(t_2) \rangle\!\rangle = -\sum_{n=1}^{\infty} n\kappa_{nm}(t_2, t_1) \tag{3.40b}$$

The correlation functions κ_{nG} and κ_{Gm} are only nonvanishing for $t_1 > 1$ and $t_2 > 1$, respectively, as a result of (3.39a), (3.39b). Similarly, the *autocorrelation function* of the gel fluctuations can be written as

$$\kappa_{GG}(t_2, t_1) \equiv \langle\!\langle \gamma(t_1)\, \gamma(t_2) \rangle\!\rangle = \sum_{m,n} mn\kappa_{nm}(t_2, t_1) \tag{3.41}$$

To calculate the above expressions, we consider Eq. (3.40a) first. From (3.36) and (3.37) we infer that

$$\kappa_{nG}(t_2, t_1) = -nc_n(t_2)[1 - (1 - t_1)\, M_2(t_1)] \tag{3.42}$$

Multiplication of (3.42) with $-n$ and summation over all n yields the autocorrelation function κ_{GG}:

$$\kappa_{GG}(t_2, t_1) = M_2(t_2)[1 - (1 - t_1)\, M_2(t_1)] \tag{3.43}$$

Note that κ_{nG} and κ_{GG} vanish if $t_1 < 1$.

In order to calculate the correlation function κ_{Gm} in (3.40b), we consider the sum $\sum_n n\overline{\xi_n(t_2)}$, which can be expressed in terms of $\xi(t_1)$ with the use of (3.23) and (3.28) for $\chi(x, t)$. We find that

$$\begin{aligned}\sum_{n=1}^{\infty} n\overline{\xi_n(t_2)} &= \frac{\partial \chi}{\partial x}(0, t_2)\\ &= \frac{\partial \chi}{\partial x}(x_1, t_1)\, \frac{\partial x_1}{\partial x}(0, t_2)\\ &= \frac{\partial x_1}{\partial x}(0, t_2) \sum_{l=1}^{\infty} l\xi_l(t_1) e^{lx_1}\end{aligned} \tag{3.44}$$

where x_1 and $\partial x_1/\partial x$ are to be evaluated in the point $(x, t) = (0, t_2)$:

$$x_1(0, t_2) = -(t_2 - t_1)\, g(t_2) \tag{3.45a}$$

$$\frac{\partial x_1}{\partial x}(0, t_2) = 1 + (t_2 - t_1)\, M_2(t_2) \tag{3.45b}$$

The correlation function κ_{Gm} is obtained if we multiply Eq. (3.44) with $-\xi_m(t_1)$ and average over all $\xi(t_1)$. The result may be expressed in terms of the generating function $f(x, t)$ in (B.2):

$$\kappa_{Gm}(t_2, t_1) = -[1 + (t_2 - t_1)\, M_2(t_2)]\, mc_m(t_1) \left[e^{mx_1} - (1 - t_1) \frac{\partial f}{\partial x}(x_1, t_1) \right] \tag{3.46}$$

with $x_1 = x_1(0, t_2)$ given in (3.45a). The factor $\partial f/\partial x$ in (3.46) may be determined from (B.9). We know from (B.4a), in combination with (3.29a), that $x_0(x_1, t_1) = x_0(x, t)$. Consequently, one finds for x_1 in (3.45a) that $x_0(x_1, t_1) = x_0(0, t_2)$ and hence, due to (B.9), that

$$\frac{\partial f}{\partial x}(x_1, t_1) = \frac{M_2(t_2)}{1 + (t_2 - t_1)\, M_2(t_2)} \tag{3.47}$$

Finally, insertion of (3.45a) and (3.47) into (3.46) gives the following explicit result for $\kappa_{Gm}(t_2, t_1)$:

$$\begin{aligned}\kappa_{Gm}(t_2, t_1) = -mc_m(t_1)\{&[1 + (t_2 - t_1)\, M_2(t_2)]\\ &\times e^{-m(t_2 - t_1)g(t_2)} - (1 - t_1)\, M_2(t_2)\}\end{aligned} \tag{3.48}$$

Note that κ_{Gm} vanishes if $t_2 < 1$, as a result of (B.11). Furthermore, multiplication of (3.48) with $-m$ and summation over all m gives again Eq. (3.43) for κ_{GG}.

4. GENERAL INITIAL CONDITIONS

Here we study the covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ in coagulating systems, starting from general initial conditions $m_k(0)$ or $c_k(0) = m_k(0)/M$. The organization of this section is as follows. In Section 4.1 we given an *exact* expression for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in terms of their *generating function*. From the generating function we study the behavior of $\langle\langle \xi_m \xi_n \rangle\rangle$ in the following three limits:

1. The limit of large cluster sizes $(m, n \to \infty)$ with the time t fixed (Section 4.2).
2. The scaling limit, where $m, n \to \infty$ and the average cluster size $s(t) \to \infty$, with the scaling arguments $m/s(t)$ and $n/s(t)$ fixed (Section 4.3).
3. The large-time limit: $t \to \infty$, with m and n fixed (Section 4.4).

Furthermore, in Section 4.5 we study the covariances $\langle\langle \xi_m y \rangle\rangle$ and the variance $\langle\langle y^2 \rangle\rangle$ of the fluctuations in the gel mass. Finally, at the end of Section 4 we add a few remarks concerning the probability distribution $\Pi_r(\xi^{(r)}, t)$ and the correlation functions $\kappa_{nm}(t_2, t_1)$.

4.1. The Exact Solution

The covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ can be calculated from Eq. (2.20) or, equivalently, from Eq. (2.23) for $e_{mn}(t)$. The relation between e_{mn} and $\langle\langle \xi_m \xi_n \rangle\rangle$ is given in (2.21). Here we solve Eq. (2.23) for $e_{mn}(t)$ with the general initial condition

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

In order to solve Eq. (2.23), we introduce the generating function $h(x, y, t)$ of $e_{mn}(t)$:

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

The initial value of $h(x, y, t)$ is given, as a result of (4.1), by

$$h(x, y, 0) = -v(x+y); \qquad v(z) \equiv \sum_n c_n(0)\, e^{nz} \tag{4.3}$$

An equation for $h(x, y, t)$ is obtained by multiplying Eq. (2.23) with e^{mx+ny} and summing over all m and n. The result may be expressed in terms of the generating function $f(x, t)$ of $kc_k(t)$, which is defined in (B.2):

$$\frac{\partial h}{\partial t} + [1 - f(x, t)] \frac{\partial h}{\partial x} + [1 - f(y, t)] \frac{\partial h}{\partial y} = f(x, t) f(y, t) \tag{4.4}$$

The generating function $f(x, t)$ satisfies the differential equation (B.3) for all $t \geqslant 0$ and is implicitly determined by (B.4).

Equation (4.4) can be solved as follows. We transform from $h(x, y, t)$ to a new function $W(z_1, z_2, t)$, which is defined by

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

and

$$z_1 \equiv f(x, t); \qquad z_2 \equiv f(y, t) \tag{4.5b}$$

Substitution into (4.4) of (4.5a), (4.5b) gives a very simple equation for $W(z_1, z_2, t)$ namely

$$\frac{\partial}{\partial t} W(z_1, z_2, t) = z_1 z_2 \tag{4.6}$$

The solution is

$$W(z_1, z_2, t) = z_1 z_2 t + W(z_1, z_2, 0) \tag{4.7}$$

The initial value $W(z_1, z_2, 0)$ in (4.7) can be expressed in the initial value (4.3) of $h(x, y, t)$. The result is

$$W(z_1, z_2, 0) = h(x_0, y_0, 0) = -v(x_0 + y_0) \tag{4.8a}$$

where the functions $x_0(x, t)$ and $y_0(y, t)$ are implicitly defined through

$$\begin{aligned} f(x_0, 0) &\equiv z_1 = f(x, t) \\ f(y_0, 0) &\equiv z_2 = f(y, t) \end{aligned} \tag{4.8b}$$

Comparison with (B.2) and (B.4a), (B.4b) yields the following explicit expressions for x_0 and y_0:

$$\begin{aligned} x_0(x, t) &= x + tf(x, t) - t \\ y_0(y, t) &= y + tf(y, t) - t \end{aligned} \tag{4.9a}$$

Combination of Eqs. (4.5)–(4.9a) finally shows that

$$h(x, y, t) = tf(x, t)\,f(y, t) - v(x_0 + y_0) \tag{4.9b}$$

is the desired solution of (4.4).

In principle, Eqs. (4.9a), (4.9b) given an exact relation for $e_{mn}(t)$, which may be calculated from $h(x, y, t)$ by inversion of (4.2). As an example, consider *monodisperse initial conditions*, where $v(x) = f(x, 0) = e^x$. In this case one finds with the use of (B.4a), (B.4b) that $h(x, y, t)$ takes the form

$$h(x, y, t) = -(1-t)\,f(x, t)\,f(y, t) \tag{4.10}$$

and inversion of (4.10) immediately gives (3.2) as a result of the definition (B.2) of $f(x, t)$. For *general initial conditions*, the inversion of (4.2) is difficult, and the results are not transparent. For this reason we consider only the *asymptotic* properties of $e_{mn}(t)$ in the limits 1–3.

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

First we write (4.9b) in a form that is more useful for our purposes. Instead of $h(x, y, t)$ in (4.2), we consider the generating function

$$H(x, y, t) \equiv \sum_{m,n} mne_{mn}(t)\, e^{mx+ny} = \frac{\partial^2 h}{\partial x\, \partial y}(x, y, t) \tag{4.11}$$

An explicit expression for $H(x, y, t)$ may readily be obtained by differentiation of (4.9b). The result is

$$\begin{aligned} H(x, y, t) &= t\frac{\partial f}{\partial x}(x, t)\frac{\partial f}{\partial y}(y, t) - u'(x_0 + y_0)\frac{\partial x_0}{\partial x}(x, t)\frac{\partial y_0}{\partial y}(y, t) \\ &= \left[t - \frac{u'(x_0 + y_0)}{u'(x_0)\,u'(y_0)}\right]\frac{\partial f}{\partial x}(x, t)\frac{\partial f}{\partial y}(y, t) \end{aligned} \tag{4.12}$$

where we have used the definition (B.2) of $u(x)$, i.e., $u(x) = f(x, 0) = v'(x)$. The partial derivatives $\partial x_0/\partial x$ and $\partial y_0/\partial y$ have been calculated from (4.8b). Inversion of $H(x, y, t)$ in (4.12) yields an expression for $e_{mn}(t)$. Formally, the result can be written as a double contour integral in the complex plane:

$$mne_{mn}(t) = \left(\frac{1}{2\pi i}\right)^2 \oint \frac{dw_1}{w_1^{m+1}} \oint \frac{dw_2}{w_2^{n+1}}\, H(x, y, t) \tag{4.13}$$

where we have defined $w_1 \equiv e^x$ and $w_2 \equiv e^y$. The integration paths in (4.13) are closed contours circling the origin in the w_1 or w_2 plane once in the counterclockwise direction.

Equation (4.13) is a convenient starting point for calculating the behavior of $e_{mn}(t)$ at *large* values of m and n. This will be done with the use of the saddle point method. From Appendix B.2 we know for *universal* solutions $c_k(t)$ that the function $x(f, t)$, or equivalently, $w_1(f, t)$, has a saddle point at $f_s = u(x_0^s)$. The value of $x_0^s(t)$ is given in (B.16), i.e., $u'(x_0^s) = t^{-1}$. The corresponding values of $x(f, t)$ and $w_1(f, t)$ are $x_s(t) = x_0^s - tf_s + t$ and $w_s(t) = e^{x_s(t)}$. Accordingly, we calculate the *first* contour integral in (4.13) along the curve $w_1 = w_s(t) e^{i\varphi_1}$, with $-\pi < \varphi_1 \leqslant \pi$. Similarly, the *second* contour integral in (4.13) is calculated along the curve $w_2 = w_s(t)\, e^{i\varphi_2}$ with $-\pi < \varphi_2 \leqslant \pi$. As a result, for large m and n the integrand in (4.13) is sharply peaked about the point $(x, y) = (x_s(t), x_s(t))$, and only values of (x, y) close to this point contribute. Hence, substitution into (4.13) of the explicit form (4.12) of $H(x, y, t)$ gives

$$
\begin{aligned}
mne_{mn}(t) &\sim \left(\frac{1}{2\pi i}\right)^2 \left\{t - \frac{u'(2x_0^s)}{[u'(x_0^s)]^2}\right\} \\
&\quad \times \oint \frac{dw_1}{w_1^{m+1}} \frac{\partial f}{\partial x}(x, t) \oint \frac{dw_2}{w_2^{n+1}} \frac{\partial f}{\partial y}(y, t) \\
&\sim t[1 - tu'(2x_0^s)](mn)^2\, c_m(t)\, c_n(t) \qquad (m, n \to \infty) \qquad (4.14)
\end{aligned}
$$

In the first step of (4.14) we used that, at the saddle point, the values of x_0 and y_0 are given by $x_0 = y_0 = x_0^s(t)$. In the second step we used the relation (B.16) for $x_0^s(t)$ and the definition (B.2) of $f(x, t)$. The covariances $\langle\!\langle \xi_m(t)\, \xi_n(t) \rangle\!\rangle$ can be calculated from (4.14) with the use of (2.21).

An explicit expression for $e_{mn}(t)$ at large values of m and n is obtained if we substitute into (4.14) the known behavior (B.18) of $c_k(t)$ at large cluster sizes ($k \to \infty$). The result, valid in both the pre- and post-gel stages, is

$$
e_{mn}(t) \sim [1 - tu'(2x_0^s)](mn)^{-3/2}[2\pi t^2 u''(x_0^s)]^{-1}\, w_s(t)^{-(m+n)} \qquad (m, n \to \infty) \qquad (4.15)
$$

The prefactor $[1 - tu'(2x_0^s)]$ in (4.15) vanishes at the gelpoint. This follows from (B.19) and (B.16), i.e., $x_0^s(t_c) = 0$ and $t_c = [u'(0)]^{-1}$. The prefactor is *negative* in the pre-gel stage, where $t < t_c = [u'(0)]^{-1}$, and *positive* for $t > t_c$. For monodisperse initial conditions, where $u(x) = e^x$ and $x_0^s(t) = -\log t$, Eqs. (4.14) and (4.15) are in agreement with the exact solution (3.2).

4.3. The Scaling Limit

Next we show that the covariances $\langle\!\langle \xi_m(t)\, \xi_n(t) \rangle\!\rangle$ approach a *scale-invariant form* in the scaling limit, which is the limit where $m, n \to \infty$, and the average cluster size $s(t) \to \infty$, with $m/s(t)$ and $n/s(t)$ fixed. The behavior in the scaling limit of the macroscopic solution $c_k(t)$ is summarized in Appendix B.3.

We start again from Eq. (4.12) for $H(x, y, t)$. The essential observation is that, in the scaling limit, the prefactor $[\cdots]$ in the right-hand side of (4.12) depends *only* on the time t, and *not* on the scaling arguments $r_1 \equiv m/s(t)$ and $r_2 \equiv n/s(t)$. This can be seen as follows. We specify our results for the choice $s(t) \equiv M_3(t)/M_2(t)$, but different choices for the definition of "average cluster size" would change only numerical values, and not the essence of our results. From (B.27a), (B.27b) we know that in the scaling limit x_0 vanishes proportional to $-s(t)^{-1/2}$, and similarly $y_0 \propto -s(t)^{-1/2} \to 0$. We also know, from (B.24), that x_0^s vanishes: $x_0^s(t) \propto s(t)^{-1/2}$ as $t \uparrow t_c$ and $x_0^s(t) \propto -s(t)^{-1/2}$ as $t \downarrow t_c$. Therefore, the prefactor $[\cdots]$ in (4.12) can be expanded about x_0^s. In order to do this, we note that

$$\begin{aligned} u'(x_0+y_0) &= u'(x_0^s) + (x_0+y_0-x_0^s)\,u''(x_0^s) + \cdots \\ u'(x_0) &= u'(x_0^s) + (x_0-x_0^s)\,u''(x_0^s) + \cdots \\ u'(y_0) &= u'(x_0^s) + (y_0-x_0^s)\,u''(x_0^s) + \cdots \end{aligned} \tag{4.16}$$

Insertion of (4.16) into (4.12) yields for $H(x, y, t)$

$$H(x, y, t) = -\frac{u''(0)}{[u'(0)]^2}\, x_0^s(t)\, \frac{\partial f}{\partial x}(x, t)\, \frac{\partial f}{\partial y}(y, t) + \cdots \qquad (t \to t_c) \tag{4.17}$$

where we have used Eq. (B.16) for $x_0^s(t)$. A *scaling law* for the generating function $H(x, y, t)$ is obtained if we insert into (4.17) the result (B.24) for x_0^s and (B.22a), (B.22b) for $\partial f/\partial x$ and $\partial f/\partial y$. One finds that, in the scaling limit (S), $s(t)^{-1/2}\, H(x, y, t)$ approaches a *scale-invariant form* as follows:

$$s(t)^{-1/2}\, H(x, y, t) \xrightarrow{\text{S}} \mp [(2\pi)^{1/2} B]^{-1}\, h(\rho_1)\, h(\rho_2) \tag{4.18a}$$

where the parameter B is defined in (B.21b). The scaling variables ρ_1 and ρ_2 are related to x and y through

$$\rho_1 \equiv -xs(t); \qquad \rho_2 \equiv -ys(t) \tag{4.18b}$$

and $h(\rho)$ is defined in (B.22b). The minus sign in (4.18a) applies in the pre-gel stage. The plus sign applies for $t > t_c$.

A *scaling law for* $e_{mn}(t)$ can readily be obtained by inversion of (4.17). With the use of the definition (4.11) of $H(x, y, t)$ and (B.2) of $f(x, t)$ one finds that

$$mne_{mn}(t) \xrightarrow{\text{S}} \mp [(2\pi)^{1/2} B]^{-1}\, s(t)^{-1/2} (mn)^2\, c_m(t)\, c_n(t) \tag{4.19}$$

or, with the use of the scaling form (B.20) for $c_k(t)$,

$$e_{mn}(t) \xrightarrow{S} \mp [(2\pi)^{1/2} B]^{-1} s(t)^{-7/2} r_1 r_2 \varphi(r_1)\, \varphi(r_2) \tag{4.20a}$$

The scaling arguments r_1 and r_2 in (4.20a) are defined as

$$r_1 \equiv m/s(t); \qquad r_2 \equiv n/s(t) \tag{4.20b}$$

The explicit form of $\varphi(r)$ is given in (B.21a), (B.21b). Finally, a scaling law for the covariances can be found from (2.21):

$$\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$$

$$\xrightarrow{S} s(t)^{-7/2} [\delta(r_1 - r_2)\, \varphi(r_1) \mp [(2\pi)^{1/2} B]^{-1} r_1 r_2 \varphi(r_1)\, \varphi(r_2)] \tag{4.21}$$

where the Kronecker delta in (2.21) has been replaced by $s(t)^{-1}\, \delta(r_1 - r_2)$. Equation (4.21) clearly shows that in the scaling limit the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ approach a scaling form, independent of the details of the initial distribution $c_k(0)$.

4.4. The Large-Time Limit ($t \to \infty$)

From Appendix B.4 we know that in the limit $t \to \infty$

$$x_0(x, t) \to -\infty; \qquad y_0(y, t) \to -\infty \qquad (t \to \infty) \tag{4.22}$$

As a consequence, one has $u'(x_0) \sim c_1(0)\, e^{x_0}$ and hence, from (4.12),

$$H(x, y, t) \sim \{[c_1(0)t - 1]/c_1(0)\} \frac{\partial f}{\partial x}(x, t) \frac{\partial f}{\partial y}(y, t) \qquad (t \to \infty) \tag{4.23}$$

The large-time behavior of $e_{mn}(t)$ follows from inversion of (4.23). The result is

$$e_{mn}(t) \sim \{[c_1(0)t - 1]/c_1(0)\}\, mn c_m(t)\, c_n(t) \qquad (t \to \infty) \tag{4.24}$$

The large-time behavior of the concentrations $c_k(t)$ is given in (B.31). The covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ can be calculated from (2.21).

4.5. Fluctuations in the Gel Mass

We first consider the covariances $\langle\langle \xi_m \gamma \rangle\rangle$ and then the variance $\langle\langle \gamma(t)^2 \rangle\rangle$. An *exact expression* for the covariances can be obtained in terms of the generating function $H(x, y, t)$ in (4.11) as follows. We rewrite $\langle\langle \xi_m \gamma \rangle\rangle$ in terms of $e_{mn}(t)$:

$$\begin{aligned}\langle\langle \xi_m(t)\, \gamma(t) \rangle\rangle &= -\sum_n n \langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle \\ &= -\left[\sum_n n e_{mn}(t) + m c_m(t)\right] \end{aligned} \tag{4.25a}$$

and we express $\sum_n n e_{mn}$ as a contour integral in the complex plane:

$$\sum_n n e_{mn}(t) = \frac{1}{2\pi m i} \oint \frac{dw_1}{w_1^{m+1}}\, H(x, 0, t) \tag{4.25b}$$

Combination of (4.25a), (4.25b) then gives the desired result. For $t < t_c$, where there is no gel, the right-hand side of (4.25b) vanishes. To see this, we note that in the pre-gel stage $x_0(0, t) = 0$, so that

$$H(x, 0, t) = (t - t_c)\, M_2(t) \frac{\partial f}{\partial x}(x, t) = -\frac{\partial f}{\partial x}(x, t) \qquad (t < t_c) \tag{4.26}$$

We have used Eq. (B.11) for $M_2(t)$ if $t < t_c$. The fact that $\langle\langle \xi_m \gamma \rangle\rangle$ vanishes in the pre-gel stage then follows from combination of (4.25a), (4.25b), (4.26), and the definition (B.2) of $f(x, t)$.

The asymptotic behavior of $\langle\langle \xi_m \gamma \rangle\rangle$ for *large cluster sizes* $(m \to \infty)$ can be calculated along similar lines as the behavior (4.14) of $e_{mn}(t)$. The main contribution to the integral in (4.25b) comes from the region where $x \simeq x_s(t)$, or $x_0(x, t) \simeq x_0^s(t)$, so that for large m, Eq. (4.25b) reduces to

$$\sum_n n e_{mn}(t) \sim \left[t - \frac{u'(x_0^s + x_0(0, t))}{u'(x_0^s)\, u'(x_0(0, t))}\right] M_2(t)\, m c_m(t) \qquad (m \to \infty) \tag{4.27}$$

Insertion of (4.27) into (4.25a) gives the desired large-m behavior of $\langle\langle \xi_m \gamma \rangle\rangle$, namely

$$\begin{aligned}&\langle\langle \xi_m(t)\, \gamma(t) \rangle\rangle \\ &\quad \sim -m c_m(t) \left\{1 + t M_2(t) \left[1 - \frac{u'(x_0^s + x_0(0, t))}{u'(x_0(0, t))}\right]\right\} \qquad (m \to \infty)\end{aligned} \tag{4.28}$$

where we have used the definition (B.16) of $x_0^s(t)$. Note that the right-hand side of (4.28) vanishes if $t < t_c$.

The behavior of the covariances $\langle\langle \xi_m \gamma \rangle\rangle$ in the *scaling limit* [$m \to \infty$, $s(t) \to \infty$, with $r_1 = m/s(t)$ fixed] can most easily be calculated from

Eq. (4.21) for $t > t_c$. Multiplication of (4.21) with $-n$ and summation over all n gives

$$\langle\langle \xi_m \gamma \rangle\rangle \xrightarrow{\mathrm{S}} -s(t)^{-3/2} \int_0^\infty dr_2\, r_2 \{\delta(r_1 - r_2)\, \varphi(r_1) + [(2\pi)^{1/2} B]^{-1} r_1 r_2 \varphi(r_1)\, \varphi(r_2)\} \tag{4.29}$$

Calculation of the integral in (4.29) with the use of the explicit form (B.21a), (B.21b) of the scaling function $\varphi(r)$ gives

$$\begin{aligned}\langle\langle \xi_m(t)\, \gamma(t) \rangle\rangle &\xrightarrow{\mathrm{S}} -2s(t)^{-3/2} r_1 \varphi(r_1) \\ &\xrightarrow{\mathrm{S}} -2mc_m(t) \qquad (t > t_c)\end{aligned} \tag{4.30}$$

Equation (4.30) implies that, at the gelpoint t_c, the covariances $\langle\langle \xi_m \gamma \rangle\rangle$ jump from zero (for $t < t_c$) to a finite value (for $t > t_c$). This finite value is given by the right-hand side of (4.30) if m is sufficiently large.

The large-time behavior of $\langle\langle \xi_m \gamma \rangle\rangle$ can be determined from (4.25a) and (4.24). The first term on the right in (4.25a) is exponentially small compared to the second term. As a result one finds that

$$\langle\langle \xi_m(t)\, \gamma(t) \rangle\rangle \sim -mc_m(t) \qquad (t \to \infty) \tag{4.31}$$

with $c_m(t)$ given in (B.31).

Finally, the variance $\langle\langle \gamma(t)^2 \rangle\rangle$ can readily be expressed in terms of $H(x, y, t)$ with the use of the definition (2.21) of $e_{mn}(t)$. The result is

$$\langle\langle \gamma(t)^2 \rangle\rangle = \sum_{n,m} nm(e_{nm} + \delta_{nm} c_m) = H(0, 0, t) + M_2(t) \tag{4.32a}$$

where $H(0, 0, t)$ follows from (4.12) as

$$H(0, 0, t) = \left[t - \frac{u'(2x_0(0, t))}{[u'(x_0(0, t))]^2} \right] [M_2(t)]^2 \tag{4.32b}$$

An approximate expression for $\langle\langle \gamma^2 \rangle\rangle$ as $t \downarrow t_c$ can be obtained from (4.30) by multiplying with $-m$ and summing over all m:

$$\begin{aligned}\langle\langle \gamma(t)^2 \rangle\rangle &\sim 2M_2(t) \\ &\sim 2(t - t_c)^{-1} \qquad (t \downarrow t_c)\end{aligned} \tag{4.33}$$

Similarly, the behavior of $\langle\langle \gamma(t)^2 \rangle\rangle$ as $t \to \infty$ can be determined from (4.30). The result is

$$\langle\langle \gamma(t)^2 \rangle\rangle \sim c_1(t) \sim c_1(0) e^{-t} \qquad (t \to \infty) \tag{4.34}$$

Equation (4.34) clearly shows that the fluctuations in the gel mass are very small at large times, when the sol phase is virtually depleted.

Before concluding this section, we discuss the calculation of the probability distribution $\Pi_r(\boldsymbol{\xi}^{(r)}, t)$ and the correlation functions $\kappa_{nm}(t_2, t_1)$. In Section 4.1 we gave an exact expression for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ in terms of the generating function $h(x, y, t)$ or, equivalently, $H(x, y, t)$. *In principle*, for a given initial state $c_k(0)$ $(k = 1, 2,\ldots)$, the generating functions can be inverted to yield an explicit expression for $\langle\langle \xi_m \xi_n \rangle\rangle$. This determines the matrix Ξ in (2.16) and hence $\Pi_r(\boldsymbol{\xi}^{(r)}, t)$ in (2.17). Similarly, the correlation functions $\kappa_{nm}(t_2, t_1)$ can be calculated from (3.35a), where $Y_{nl}(t_2, t_1)$ must be determined from (3.31b) in combination with (3.29b). Therefore, in principle, the calculations of Sections 3.2 and 3.3 may be repeated for general initial conditions. *In practice*, this task may not always be easy.

5. IMPLICATIONS AND EXTENSIONS

In this paper we have applied van Kampen's Ω-expansion to the master equation in the form (2.2), with rate constants $K_{ij} = ij$. From the lowest order in the expansion we find that the concentrations $c_k(t)$ satisfy the macroscopic law (1.8) for all $t \geqslant 0$. From the next order in the Ω-expansion we find a linear Fokker–Planck equation for the marginal probability distribution $\Pi_r(\boldsymbol{\xi}^{(r)}, t)$ of the fluctuations $\boldsymbol{\xi}^{(r)} = (\xi_1,\ldots, \xi_r)$ in the numbers of clusters of size $k \leqslant r$. The solution of the Fokker–Planck equation has the form of a multivariate Gaussian distribution with zero mean, $\langle \boldsymbol{\xi}^{(r)} \rangle = \mathbf{0}$, and covariance matrix $\Xi_{mn} = \langle\langle \xi_m \xi_n \rangle\rangle$ $(m, r \leqslant r)$.

Concerning the status of the Ω-expansion, the following is known. For large systems, i.e., in the limit $M \to \infty$, the validity of the Gaussian approximation (2.17), and hence of the Fokker–Planck equation (2.13), has been proved by Kurtz$^{(15)}$ for a finite number of reactants and an arbitrary but finite time interval $[0, T]$. This result is applicable to the master equation in the form (2.2), since in this case the number of reactants is $r + 1$, which is finite. The $r + 1$ reactants are the k-mers (with $k = 1,\ldots, r$) and, as an $(r + 1)$th reactant, the mass G_r contained in clusters of size $k > r$. Hence we infer that the results of this paper are rigorously correct, at least for finite values of r and a given time interval $[0, T]$, in the limit of a large system $(M \to \infty)$.

Next, we discuss the *behavior of the fluctuations* as a function of time. One of the remarkable results of this paper is that, for general initial conditions, the equal-time correlation functions or covariances $\langle\langle \xi_m(t)\, \xi_n(t) \rangle\rangle$ are analytical functions of the time for all $t \geqslant 0$ and all $m, n = 1, 2,\ldots$. In particular, this implies that the variances $\langle\langle \xi_m(t)^2 \rangle\rangle$ remain finite at the gelpoint t_c. In fact, the only fluctuations that become *large* near t_c are the fluctuations in the *gel mass.* Equation (4.33) shows that the variance $\langle\langle y(t)^2 \rangle\rangle$ diverges as $t \downarrow t_c$ proportional to the second moment $M_2(t) \sim (t-t_c)^{-1}$.

Yet, the fluctuations in the concentrations of *finite-size clusters* also become important in the vicinity of the gelpoint. To see this, we consider the *moments* $M_{\alpha\beta}$ of the occupation numbers m_k, which are defined as

$$M_{\alpha\beta} \equiv \sum_{k,l} k^\alpha l^\beta m_k m_l \tag{5.1}$$

The average value of $M_{\alpha\beta}$ can be split in a macroscopic part, determined by the averages $\langle m_k \rangle$, and a part due to fluctuations as follows:

$$\langle M_{\alpha\beta} \rangle = \sum_{k,l} k^\alpha l^\beta \langle m_k \rangle \langle m_l \rangle + \sum_{k,l} k^\alpha l^\beta \langle\langle m_k m_l \rangle\rangle \tag{5.2}$$

The ratio $R(t)$ of the second and the first terms on the right in (5.2) defines a measures for the influence of the fluctuations on the value of $M_{\alpha\beta}$. With the use of (1.11) one finds that, for large M, this ratio is equal to

$$\begin{aligned} R(t) &\equiv \sum_{k,l} k^\alpha l^\beta \langle\langle m_k m_l \rangle\rangle \Big/ \sum_{k,l} k^\alpha l^\beta \langle m_k \rangle \langle m_l \rangle \\ &\sim M^{-1} \sum_{k,l} k^\alpha l^\beta \langle\langle \xi_k \xi_l \rangle\rangle / M_\alpha(t)\, M_\beta(t) \qquad (M \to \infty) \end{aligned} \tag{5.3}$$

Therefore, at a finite distance from the gelpoint t_c, the ratio $R(t)$ is of the order of M^{-1}, which is always small if M is large.

However, for a fixed value of M the ratio $R(t)$ becomes large if t approaches the gelpoint t_c. This can be seen from the scaling function results (4.21) for $\langle\langle \xi_k \xi_l \rangle\rangle$ and (B.20) for $c_k(t)$. One finds that as $t \to t_c$

$$R(t) \sim C_{\alpha\beta} M^{-1} s(t)^{3/2} \qquad (M \gg 1, \quad t \to t_c) \tag{5.4}$$

where $C_{\alpha\beta}$ is some constant and $s(t)$ is the average cluster size, given in (B.23). In the derivation of (5.4) we have approximated the sums in (5.3) by integrals, which is allowed if $\alpha > 3/2$ and $\beta > 3/2$. The fluctuations in $M_{\alpha\beta}$ become important as soon as $R(t) \simeq 1$. From (5.4) it follows that this happens if $s(t) \simeq M^{2/3}$ or $|t_c - t| \simeq M^{-1/3}$. We conclude that a macroscopic (Smoluchowski-type) description of the moments $M_{\alpha\beta}$ is justifiable only if the distance from the gelpoint is sufficiently large: $M^{1/3} |t_c - t| \gg 1$. The physical explanation for this is that the main contribution to the higher moments comes from *large* clusters, with $k \gtrsim s(t)$, and the number of such clusters is of the order of unity if $s(t) \simeq M^{2/3}$. It follows that for

$|t_c - t| \lesssim M^{-1/3}$ the fluctuations in the number of large clusters become very large, so that the Ω-expansion of the moments $M_{\alpha\beta}$ breaks down.

Another limit where the fluctuations in the concentrations of sol clusters become important is the limit of *large times.* In this limit the absolute size of the fluctuations becomes small, as can be seen from Eqs. (4.21) and (B.31). However, the *relative* size of the fluctuations, i.e., the value of $R(t)$ defined in (5.3), becomes very large if $t \to \infty$. It follows from (2.21), (4.24), (B.31), (B.12b), and (B.14b) that monomers are the dominant species in the sol, and that only terms with $k = l = 1$ contribute to $R(t)$ in (5.3) in the long-time limit. Thus, one finds that $R(t) \sim [Mc_1(t)]^{-1} \sim e^t/Mc_1(0)$. The size of the fluctuations becomes large if $R(t) \simeq 1$, which happens if $t \simeq t_M \equiv \log[Mc_1(0)]$. The importance of the fluctuations for $t \simeq t_M$ is quite obvious, since at this stage the sol contains only a single monomer: $\langle m_k \rangle \simeq Mc_1(t) \simeq 1$. The breakdown of the Gaussian approximation at $t \simeq t_M$ is a nice illustration of the fact that Kurtz's proof of the validity of this method cannot be extended to time intervals $[0, T_M]$, where T_M increases proportional to $\log M$ as $M \to \infty$.

At a technical level, one of the most curious facts of this paper is the drastic simplification occurring in Eq. (2.20) for the covariances $\langle\langle \xi_k \xi_l \rangle\rangle$, as a result of the introduction of e_{kl} in (2.21). This suggests that e_{kl} rather than $\langle\langle \xi_k \xi_l \rangle\rangle$ is the quantity of physical interest. The interpretation of e_{kl} is as follows. In the same way as $\langle\langle \xi_k \xi_l \rangle\rangle$ is related to the covariances (or second *cumulants*) of the occupation numbers m_k, i.e.,

$$\langle\langle m_k m_l \rangle\rangle \sim M \langle\langle \xi_k \xi_l \rangle\rangle \qquad (M \to \infty) \tag{5.5a}$$

one finds that e_{kl} is related to the second *factorial cumulants* $[m_k m_l]$, which are defined as

$$\begin{aligned} [m_k m_l] &\equiv \langle\langle m_k m_l \rangle\rangle - \delta_{kl} \langle m_k \rangle \\ &\sim M e_{kl}(t) \qquad (M \to \infty) \end{aligned} \tag{5.5b}$$

The importance of the factorial cumulants $[m_k m_l]$ is that the second (and higher) factorial cumulants *vanish* (Ref. 1, Section I.2) if each number m_k is taken from a *Poisson distribution* and all m_k, m_l are statistically independent. The relevance of this property is particularly clear in the exact solution (A.7) of the master equation for monodisperse initial conditions. Equation (A.7) shows that, apart from a factor $\Delta(\sum_j jm_j, M)$ representing the mass conservation law, the variables m_k are mutually independent, satisfying Poisson statistics with the average $\langle m_k \rangle \sim Mc_k(t)$ $(k = 1, 2,...)$. Without the restriction $\sum_j jm_j = M$ one would have $e_{kl}(t) = 0$ for all $t \geqslant 0$. Conversely, we infer that the central role of e_{kl} in this paper is a *reflection of the conservation law for the total mass.*

We consider the role of the factorial cumulants e_{kl} in some more detail. In particular, we consider the *sign of* e_{kl} in the pre-gel and in the post-gel stage. From (3.2) we know that for monodisperse initial conditions the sign of e_{kl} is negative in the pre-gel stage and positive in the post-gel stage. This implies that, as a result of the mass conservation law, the fluctuations obey *sub-Poisson* and *super-Poisson* statistics for $t<1$ and $t>1$, respectively. The interpretation of this fact for the off-diagonal elements $e_{kl}(t)$ (with $k \neq l$) is given below (3.4). The interpretation for the diagonal elements $e_{kl}(t)$ is as follows. Suppose that the number of k-mers at time t_1 exceeds the average, i.e., that $\xi_k(t_1)>0$. The return of the average fluctuation $\langle \xi_k(t) \rangle$ to its limiting value $\langle \xi_k \rangle = 0$ is described by Eq. (3.22). The second term on the right in (3.22) corresponds to pure Poisson statistics. The first term on the right reflects the mass conservation law, since it shows that k-mers and smaller polymers are *not* statistically independent. In the pre-gel stage this first term is *negative*, since an excess of k-mers implies that there are fewer j-mers, i.e., $\langle \xi_j \rangle$ is negative. As a result, the probability distribution for ξ_k is narrower than the Poisson distribution (sub-Poisson statistics). In the post-gel stage an excess of k-mers implies that, most likely, the sol phase as a whole is larger, so that the first term on the right in (3.22) is positive (super-Poisson statistics). These arguments are also true for general initial conditions. In this case the fact that e_{kl} has a different sign in the pre-gel and in the post-gel stage is most clearly demonstrated by Eqs. (4.15) and (4.19).

We conclude with some comments on the macroscopic law (1.8) for the coagulation model $K_{ij} = ij$ obtained by applying the Ω-expansion to the master equation (1.2). Equation (1.8) differs from Smoluchowski's equation (1.1) in the post-gel stage because the sol mass $\sum jc_j$ in the last term is replaced by unity. This difference shows up for $t>t_c$, where $\sum jc_j < 1$, and corresponds to differences in the description of interactions between the sol and the gel. The post-gel coagulation model (1.8), referred to as the F-model in the terminology of Ziff *et al.*,(12) includes sol–gel interactions, as discussed below Eq. (1.8). On the other hand, in Smoluchowski's equation (1.1), referred to in Ref. 12 as the S-model, interactions between the sol and the gel are absent. Here we comment on this alternative model for the post-gel stage, where sol–gel reactions are not taken into account. We start with the observation that the reduced reactivity of the "gel" in the S-model must be a property of *all large clusters.* The reason is simply that a gel (in the sense of infinite cluster) does not occur in a physical (finite) system, i.e., that in practice "gel" means "large cluster." Moreover, all physical mechanisms conceived to explain the reduced gel reactivity(9,16) apply for all large clusters.

Therefore, suppose that the reactivity is reduced (say, zero) for all clusters larger than size k_0. In this case application of the Ω-expansion to the master equation (1.2) immediately gives the following macroscopic law for $k \leqslant k_0$ and all $t \geqslant 0$:

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{k_0} K_{kj} c_j \qquad (k \leqslant k_0) \tag{5.6}$$

Equation (5.6) has been solved by Lushnikov and Piskunov(16) for various choices of the rate constants, including $K_{ij} = ij$. The model (5.6) has been baptized "finite Smoluchoski kinetics" by Leyvraz,(17) who solves the case $K_{ij} = \text{const}$. Thus, we arrive at the following conclusion. From the point of view of the Ω-expansion the S-model (1.1) is *not* the correct macroscopic law in the post-gel stage. One *cannot* study the fluctuations in the S-model. The S-model is merely an approximation of the finite Smoluchowski kinetics (5.6), and this approximation is better for larger values of k_0.

In this paper we have studied the fluctuations from a master equation describing *irreversible* coagulation. Next we comment on the possible generalization of this paper to *reversible* aggregation processes. A master equation describing both coagulation and fragmentation has been proposed by Hendriks.(18) In order to describe breakup of clusters this author adds a term to the right-hand side of Eq. (1.2), of the form

$$\tfrac{1}{2} \sum_{i,j} \Delta_{ij}^{-} [F_{ij} m_{i+j} P(\mathbf{m}, t)] \tag{5.7a}$$

where F_{ij} is a fragmentation rate and Δ_{ij}^{-} is a difference operator:

$$\Delta_{ij}^{-} f(\mathbf{m}) \equiv f(\{m_k - \delta_{ik} - \delta_{jk} + \delta_{i+j,k}\}) - f(\mathbf{m}) \tag{5.7b}$$

The essential point in (5.7a), (5.7b) is that the breakup rates F_{ij} depend *only* on the cluster sizes i and j.

Unfortunately, for the model considered in this paper, a description of the combined coagulation–fragmentation process merely in terms of cluster sizes, as in (5.7a), (5.7b), is impossible. The reason for this has been discussed in Ref. 19: the fragmentation rate for the breakup of k-mers into i- and j-mers (with $i + j = k$) depends not only on the cluster sizes, but also on the specific configurations μ, ν, ρ of the i-, j-, and k-mers. Therefore, one should specify the configurations separately, and construct a master equation in terms of the occupation numbers $m_{k\rho}$ and the fragmentation rates $F^{\rho}_{i\mu j\nu}$. The *average* fragmentation rate F_{ij} is then given by

$$F_{ij} = \left(\sum_{\mu,\nu,\rho} F^{\rho}_{i\mu j\nu} m_{k\rho} \right) \Big/ \sum_{\rho} m_{k\rho} \tag{5.8}$$

Equation (5.8) shows that in our model the fragmentation rate F_{ij} is a *stochastic variable.* Moreover, in a large system ($M \to \infty$), the fluctuations in F_{ij} are of the same order as the fluctuations in m_{kp}, i.e., of relative order $M^{-1/2}$. This shows that in our model F_{ij} can never be treated as a fragmentation *constant.* This conclusion, that F_{ij} cannot be treated as a constant, can be generalized to all models for the formation of branched polymers. In fact, the only physical model for which a description of the form (5.7) can be used is the constant kernel, $K_{ij} = F_{ij} = 1$, which corresponds to the formation of linear chains.(7)

Next we comment on the work of Donoghue,(20,21) who has studied the *equilibrium solution* of the combined coagulation–fragmentation process for the classical polymerization models RA_f of Flory and Stockmayer. The relevance of Donoghue's results for the present work is that, in the limit $f \to \infty$, the coagulation rates K_{ij} in the model RA_f reduce to our model (1.7). The essential difference of course is that in our model fragmentation does not occur. For convenience we take the limit $f \to \infty$ in Donoghue's results.

Donoghue(20) finds that, in the pre-gel stage, the equilibrium concentrations $c_k \equiv \lim_{M \to \infty} \langle m_k \rangle / M$ have the *same* form as the time-dependent solution of the kinetic equation (1.8) for monodisperse initial conditions, which is given in Eq. (1.9). However, in the post-gel stage he finds that c_k has the form

$$c_k = A k^{k-2}/(k!\, e^k) \sim A(2\pi)^{-1/2} k^{-5/2} \qquad (k \to \infty) \tag{5.9}$$

where A is equal to the sol fraction, i.e., $A = \sum_{k=1}^{\infty} k c_k < 1$. The result (5.9) differs from the form (1.9), since Eq. (1.9) predicts that c_k falls off exponentially as a function of k, rather than algebraically, if $t > 1$.

The discrepancy between the kinetic and the equilibrium theory has caused some confusion. First, in Ref. 20 it is suggested that the kinetic interpretation of the S-model(22) that the gel is inactive may not be correct. Furthermore, Donoghue(21) constructs an alternative "kinetic" equation, in agreement with the equilibrium solutions. For $K_{ij} = ij$ this alternative equation is different from Eq. (1.8) and also different from the S-model. The present paper shows that the correct kinetic equation for the model $K_{ij} = ij$ is Eq. (1.8). Furthermore, the discussion around Eq. (5.6) shows that the kinetic interpretation of the S-model given by Ziff and Stell(22) is basically correct. There is, however, no dynamic or kinetic basis for Donoghue's construction of a "kinetic" equation. His alternative does not seem to have any relevance for a description of the size distribution in time-dependent coagulation phenomena. Donoghue's implicit assumption that the kinetic and the equilibrium solutions must have the same form as a function of k is *not* justified in the post-gel stage.

We comment on the possible extension of the methods used in this paper to other models. For general reaction rates K_{ij} one cannot, as a rule, construct a closed master equation for the marginal probability density $P_r(\mathbf{m}^{(r)}, t)$ as was done in (2.2). For this reason we applied the Ω-expansion to the master equation (1.2) and found two other (nongelling) models where the fluctuations can be studied in detail for general initial conditions. These models are $K_{ij} = i + j$ and $K_{ij} = 1$. Furthermore, we obtained some qualitative results for general homogeneous kernels. These results will be published in a subsequent paper.

Before concluding this paper, we summarize the main results. The coagulation model presented here is one of the few nontrivial[5] nonlinear kinetic equations for which the fluctuations can be calculated exactly. Explicit results were obtained for *monodisperse initial conditions*, $c_k(0) = \delta_{k1}$. In this case one finds a relatively simple form for $\Xi(t)$, namely $\Xi_{mn} = \delta_{mn} c_n - (1-t)\, mnc_m c_n$, and, as a result, $\Pi_r(\xi^{(r)}, t)$ can be calculated explicitly. Furthermore we calculated the two-time correlation functions $\langle\langle \xi_m(t_1)\, \xi_n(t_2) \rangle\rangle$, with $t_1 \leqslant t_2$, for all $n, m = 1, 2, \ldots$. For *general initial conditions* we found an exact expression for the covariances $\langle\langle \xi_m \xi_n \rangle\rangle$ and $\langle\langle \xi_m \gamma \rangle\rangle$ in terms of their generating function. From the generating function we calculated the asymptotic behavior of $\langle\langle \xi_m \xi_n \rangle\rangle$ and $\langle\langle \xi_m \gamma \rangle\rangle$ in the limit of large cluster sizes ($n, m \to \infty$), in the scaling limit, and in the limit of large times ($t \to \infty$). In these limits the form of the covariances is relatively simple, and does not depend on the details of the initial distribution. An important implication of these results is that the macroscopic (Smoluchowski-type) description breaks down in the vicinity of the gelpoint, namely if $|t_c - t| \simeq M^{-1/3}$, and also at large times, for $t \gtrsim \log[Mc_1(0)]$. Another interesting observation is that the relation (4.33) between the fluctuations in the gel fraction (order parameter) and the second moment of the size distribution, which is a well-known result in the theory of continuous phase transitions,[(24)] has been extended here to a nonequilibrium phase transition.

APPENDIX A

In this appendix we summarize and extend the results of Lushnikov[(6)] concerning the *exact solution* of the master equation (1.2) for $K_{ij} = ij$ and a monodisperse initial state. We give explicit expressions for the average number of clusters $\langle m_k \rangle$ and the covariances $\langle\langle m_i m_j \rangle\rangle$. We also discuss the limit of a large system, i.e., $M \to \infty$. The body of the paper deals with approximate or asymptotic solutions for $M \to \infty$.

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[5] Another, somewhat trivial, example is McKean's model-Boltzmann equation, which is discussed by van Kampen.[(23)]

First we discuss Lushnikov's exact solution for monodisperse initial conditions. The exact solution is not formulated in terms of the probability distribution $P(\mathbf{m}, t)$ itself. Instead, Lushnikov derives an expression for the generating function $\hat{P}(\mathbf{x}, t)$ of $P(\mathbf{m}, t)$ that is defined as

$$\hat{P}(\mathbf{x}, t) \equiv \sum_{\mathbf{m}} P(\mathbf{m}, t) \exp(\mathbf{m} \cdot \mathbf{x}) \tag{A.1}$$

Note that the summand in (A.1) vanishes unless $\sum km_k = M$. This is a consequence of the mass conservation law (1.4). Lushnikov has shown that $\hat{P}(\mathbf{x}, t)$ is exactly given by the following contour integral in the complex plane:

$$\hat{P}(\mathbf{x}, t) = \frac{M!}{2\pi i} \oint dz\, z^{-M-1} \exp\left[\sum_{k=1}^{M} a_k(t) z^k \exp(x_k)\right] \tag{A.2}$$

where $a_k(t)$ satisfies a set of differential equations

$$M\dot{a}_k = \tfrac{1}{2} \sum_{i+j=k} ija_i a_j + \tfrac{1}{2}(k-M)\, ka_k \qquad (k = 1,..., M) \tag{A.3}$$

that is to be solved with the initial condition $a_k(0) = \delta_{k1}$. The path of integration in (A.2) is a closed contour circling the origin in the complex z plane once in the counterclockwise direction. In other words, apart from a factor $M!$, $\hat{P}(\mathbf{x}, t)$ is the coefficient of z^M in the Taylor expansion of the integrand in (A.2).

Equation (A.3) can be solved in terms of the generating function

$$G(z, t) \equiv \sum_{k=1}^{M} a_k(t) z^k \tag{A.4}$$

An explicit expression for $G(z, t)$, or rather for $\exp[G(z, t)]$, can be obtained from (A.3) in the form of a power series in z. The result is(6)

$$\exp[G(z, t)] = 1 + u(z, t) + O(z^{M+1}) \tag{A.5}$$

where $u(z, t)$ is a polynomial of order M:

$$u(z, t) \equiv \sum_{n=1}^{M} q_n(t)\, z^n \tag{A.6a}$$

and $q_n(t)$ is defined as

$$q_n(t) \equiv (1/n!) \exp[-\tfrac{1}{2}nt(1 - n/M)] \tag{A.6b}$$

Note that the precise structure of the term of order z^{M+1} in (A.5) is irrelevant, since the coefficients $a_k(t)$ in $G(z, t)$ are completely determined by the coefficients $q_n(t)$ in $u(z, t)$, and vice versa.

Lushnikov's results (A.1)–(A.6) in terms of generating functions can be used to construct *explicit expressions* for the probability distribution $P(\mathbf{m}, t)$ as follows. The structure of the solution can be determined$^{(7)}$ by expanding the integrand in (A.2) in powers of z and selecting the coefficient of $z^M \exp(\mathbf{m}\cdot\mathbf{x})$. The result is

$$P(\mathbf{m}, t) = M! \prod_{k=1}^{M} \{[a_k(t)]^{m_k}/m_k!\}\, \Delta\left(\sum_j j m_j, M\right) \tag{A.7}$$

where $\Delta(i, j)$ is a Kronecker delta, i.e., $\Delta(i, j) = 1$ if $i = j$ and $\Delta(i, j) = 0$ otherwise. An explicit expression for $a_k(t)$, and hence for $P(\mathbf{m}, t)$, can be obtained from (A.5) by taking the logarithm on both sides and using the expansion formula for $\log(1+u)$ with $|u| < 1$. One finds that

$$\begin{aligned} G(z, t) &= \log[1 + u(z, t)] + O(z^{M+1}) \\ &= \sum_{j=1}^{M} [(-1)^{j-1}/j]\, u(z, t)^j + O(z^{M+1}) \qquad (z \to 0) \end{aligned} \tag{A.8}$$

Insertion into (A.8) of the explicit form (A.6a) of $u(z, t)$ and comparison of the coefficients of z^k on both sides of (A.8) yields the following expression for $a_k(t)$:

$$a_k(t) = \sum_{j=1}^{k} [(-1)^{j-1}/j] \sum_{n_1 + \cdots + n_j = k} q_{n_1}(t) \cdots q_{n_j}(t) \qquad (n_i \geqslant 1) \tag{A.9}$$

Thus, for all $k \leqslant M$, $a_k(t)$ is a finite sum of products of factors $q_n(t)$ $(n \leqslant k)$.

Lushnikov's results can also be used to calculate the *moments* of the probability distribution $P(\mathbf{m}, t)$. The zeroth and first moments were given in Ref. 6. The zeroth moment of $P(\mathbf{m}, t)$ can be calculated from (A.1)–(A.6). The result shows that the probability distribution is properly normalized:

$$\sum_{\mathbf{m}} P(\mathbf{m}, t) = \hat{P}(\mathbf{0}, t) = \frac{M!}{2\pi i} \oint \frac{dz}{z^{M+1}} \exp[G(z, t)] = 1 \tag{A.10}$$

The first moment of $P(\mathbf{m}, t)$ is obtained from (A.1) by differentiation with respect to x_k. The result is

$$\begin{aligned} \langle m_k(t) \rangle &= \frac{\partial \hat{P}}{\partial x_k}(\mathbf{0}, t) = a_k(t) \frac{M!}{2\pi i} \oint dz\, z^{-M+k-1} \exp[G(z, t)] \\ &= a_k(t)\, M!\, q_{M-k}(t) \end{aligned} \tag{A.11}$$

We proceed and calculate the second moments $\langle m_i m_j \rangle$, which can be obtained from the second derivative of $\hat{P}(\mathbf{x}, t)$:

$$\begin{aligned}\langle m_i m_j \rangle &= \frac{\partial^2 \hat{P}}{\partial x_i\, \partial x_j}(\mathbf{0}, t) \\ &= \delta_{ij} \langle m_i \rangle + M!\, a_i(t)\, a_j(t)\, q_{M-i-j}(t) \qquad \text{(A.12)}\end{aligned}$$

In (A.12) we have used the explicit form (A.11) of $\langle m_i(t) \rangle$. The covariances $\langle\!\langle m_i m_j \rangle\!\rangle = \langle m_i m_j \rangle - \langle m_i \rangle \langle m_j \rangle$ follow from (A.12) and (A.11) as

$$\langle\!\langle m_i m_j \rangle\!\rangle = \delta_{ij} \langle m_i \rangle + \langle m_i \rangle \langle m_j \rangle [q_{M-i-j}/(M!\, q_{M-i}\, q_{M-j}) - 1] \qquad \text{(A.13)}$$

Higher moments can be calculated straightforwardly.

Finally, we calculate approximate expressions for $\langle m_k \rangle$ and $\langle\!\langle m_i m_j \rangle\!\rangle$, valid if the system is large ($M \to \infty$). First we determine the asymptotic behavior of $a_k(t)$ as $M \to \infty$ with the use of (A.3). To do this, we transform from $a_k(t)$ to a new function $A_k(t)$, defined as

$$\begin{aligned}A_k(t) &\equiv M^{k-1} a_k(t) \exp[-\tfrac{1}{2} kt(1 - k/M)] \\ &= M^{k-1} (M-k)!\, a_k(t)\, q_{M-k}(t) \qquad \text{(A.14)}\end{aligned}$$

and we find the following equation for $A_k(t)$:

$$\dot{A}_k = \tfrac{1}{2} \sum_{i+j=k} ij A_i A_j \exp(ijt/M) - (1 - k/M)\, k A_k \qquad \text{(A.15a)}$$

$$A_k(0) = \delta_{k1} \qquad \text{(A.15b)}$$

For large M, Eq. (A.15a) reduces to

$$\dot{A}_k = \tfrac{1}{2} \sum_{i+j=k} ij A_i A_j - k A_k + O(M^{-1}) \qquad (M \to \infty) \qquad \text{(A.16)}$$

To leading order, Eq. (A.16), with the initial condition (A.15b), is identical with Smoluchowski's equation (1.8) for monodisperse initial conditions. Thus, for large M, $A_k(t)$ reduces to the concentrations $c_k(t)$ in (1.9), i.e.,

$$A_k(t) = c_k(t) + O(M^{-1}) \qquad (M \to \infty) \qquad \text{(A.17)}$$

Combination of (A.11), (A.14), and (A.17) shows that, for large M, the average number of k-mers per unit volume is equal to the solution $c_k(t)$ of the macroscopic law (1.8), which is given in Eq. (1.9):

$$M^{-1} \langle m_k(t) \rangle = c_k(t) + O(M^{-1}) \qquad (M \to \infty) \qquad \text{(A.18)}$$

Similarly, we find an asymptotic expression for the covariances (A.13) if we use Eq. (A.18) and the explicit form (A.6b) of $q_n(t)$. The result is

$$\begin{aligned} &M^{-1}\langle\!\langle m_i(t)\, m_j(t)\rangle\!\rangle \\ &\quad = c_i(t)[\delta_{ij} - (1-t)\, ijc_j(t)] + O(M^{-1}) \qquad (M \to \infty) \end{aligned} \tag{A.19}$$

Equation (A.19) implies that the size of the fluctuations around the macroscopic solution is of relative order $M^{-1/2}$, i.e., that $\langle\!\langle (m_k)^2 \rangle\!\rangle^{1/2} / \langle m_k \rangle = O(M^{-1/2})$ as $M \to \infty$.

APPENDIX B

In this appendix we review the properties for *general* initial conditions of the solution $c_k(t)$ of the macroscopic law (1.8), i.e.,

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} ijc_ic_j - kc_k \qquad (k=1, 2,...) \tag{B.1}$$

Most of the results listed in this section have been obtained by Ziff *et al.*(12) For the details we refer to their work. Here we give only a summary. We discuss first the solution of Eq. (B.1) in terms of generating functions and then, in this order, the behavior of $c_k(t)$ at large cluster sizes ($k \to \infty$), in the scaling limit, and in the limit $t \to \infty$. Finally, we discuss the special case of monodisperse initial conditions.

B.1. Solution for General Initial Conditions

Equation (B.1) can be solved with the use of the generating function $f(x, t)$ of $kc_k(t)$, which is defined as

$$\begin{aligned} f(x, t) &\equiv \sum_{k=1}^{\infty} kc_k(t)\, e^{kx} \\ u(x) &\equiv \sum_{k=1}^{\infty} kc_k(0)\, e^{kx} = f(x, 0) \end{aligned} \tag{B.2}$$

The initial distribution $c_k(0)$ is represented by the generating function $u(x)$. Insertion of (B.2) into (B.1) gives a partial differential equation for $f(x, t)$:

$$\frac{\partial f}{\partial t} + (1-f)\frac{\partial f}{\partial x} = 0; \qquad f(x, 0) = u(x) \tag{B.3}$$

The solution $f(x, t)$ of (B.3) satisfies the following implicit relation in terms of $u(x)$:

$$f(x, t) = u(x_0) \tag{B.4a}$$

where $x_0(x, t)$ is defined as

$$x_0(x, t) \equiv x + tf(x, t) - t \tag{B.4b}$$

Similarly, if $f(x, t_1) \equiv w(x)$, then $f(x, t)$ can be written as

$$f(x, t) = w(x_1) = f(x_1, t_1) \tag{B.5a}$$

with

$$x_1 = x + (t - t_1)[f(x, t) - 1] \tag{B.5b}$$

In principle, the concentrations $c_k(t)$ can be calculated from $f(x, t)$ by inversion of (B.2).

We consider the various moments of $c_k(t)$. The nth moment $M_n(t)$ is defined as

$$M_n(t) \equiv \sum_{k=1}^{\infty} k^n c_k(t) = \frac{\partial^{n-1} f}{\partial x^{n-1}}(0, t) \qquad (n = 1, 2, \ldots) \tag{B.6}$$

The *first moment* gives the fraction of the total mass contained in finite size clusters (sol particles). The gel is identified with an infinite cluster. Conservation of total mass implies that the first moment $M_1(t)$ and the gel fraction $g(t)$ are related as

$$M_1(t) + g(t) = 1 \tag{B.7a}$$

An implicit relation for $M_1(t)$, or, equivalently, $g(t)$, is obtained from (B.4) by setting $x = 0$. The result is

$$M_1(t) = u(t(M_1(t) - 1)); \qquad g(t) = 1 - u(-tg(t)) \tag{B.7b}$$

Equation (B.7b) for $M_1(t)$, or $g(t)$, has *two solutions*. The first solution, $g(t) = 0$, is valid in the pre-gel stage, i.e., before the gelpoint t_c. The second solution, satisfying $g(t) > 0$, is the relevant root in the post-gel stage, i.e., if $t > t_c$. The behavior of the second root for $t \downarrow t_c$ can be calculated by expanding (B.7b) about $g = 0$. The result is

$$g(t) \sim 2[u'(0)]^2[tu'(0) - 1]/u''(0) \equiv 2(t - t_c)/t_c^3 u''(0) \qquad (t \downarrow t_c) \tag{B.8a}$$

The gelpoint $t_c = [u'(0)]^{-1}$ has been determined from the condition $g(t_c) = 0$. For large times one finds

$$1 - g(t) \sim u(-t) \sim c_1(0)\, e^{-t} \qquad (t \to \infty) \tag{B.8b}$$

implying that, eventually, all mass is contained in the gel.

Next we consider the higher moments. The *second moment* $M_2(t)$ can be calculated from (B.6) for $n=2$, with $f(x, t)$ given by (B.4). Differentiation of (B.4a) with respect to x gives

$$\frac{\partial f}{\partial x}(x, t)=\frac{u'(x_0)}{1-tu'(x_0)} \tag{B.9}$$

implying for $M_2(t)$, because of (B.6),

$$M_2(t)=u'(-tg(t))/[1-tu'(-tg(t))] \tag{B.10}$$

In the pre-gel stage, where $g(t)=0$, Eq. (B.10) reduces to

$$M_2(t)=(t_c-t)^{-1} \qquad (t<t_c) \tag{B.11}$$

Equation (B.11) shows that $M_2(t)$ diverges at t_c. In the post-gel stage, one finds from (B.10), (B.8a), and (B.8b) that

$$M_2(t)\sim(t-t_c)^{-1} \qquad (t\downarrow t_c) \tag{B.12a}$$

$$\sim u'(-t)\sim c_1(0)\,e^{-t} \qquad (t\to\infty) \tag{B.12b}$$

Similarly, results for the *third moment* $M_3(t)$ are obtained from (B.6) with $n=3$. In the pre-gel stage one finds that

$$M_3(t)=M_3(0)(1-t/t_c)^{-3} \tag{B.13}$$

and in the post-gel stage

$$M_3(t)\sim M_3(0)(t/t_c-1)^{-3} \qquad (t\downarrow t_c) \tag{B.14a}$$

$$\sim c_1(0)\,e^{-t} \qquad (t\to\infty) \tag{B.14b}$$

Still higher moments, i.e., $M_n(t)$ with $n>3$, can be calculated analogously.

B.2. Results at Large Cluster Sizes ($k\to\infty$)

The large-k behavior of $c_k(t)$ at a fixed time t can be calculated as follows. The first step is to write $c_k(t)$ as a contour integral in the complex plane:

$$k^2c_k(t)=\frac{1}{2\pi i}\oint\frac{dw}{w^{k+1}}\frac{\partial f}{\partial x}(x, t); \qquad w\equiv e^x \tag{B.15}$$

Equation (B.15) expresses the fact that $k^2c_k(t)$ is the coefficient of $w^k=e^{kx}$ in the generating function $(\partial f/\partial x)(x, t)$. The integration path in (B.15) circles the origin in the complex w plane once, and counterclockwise. The second step is to approximate the integral in (B.15) for large k with the use of the saddlepoint method. It is readily seen from (B.9) that the function $x(f, t)$ has a saddle point at $f_s = u(x_0^s)$, where x_0^s is implicitly defined through

$$u'(x_0^s) = t^{-1} \tag{B.16}$$

The corresponding values of $x(f, t)$ and $w(f, t)$ at the saddle point are

$$x_s(t) = x_0^s - tf_s + t; \qquad w_s(t) = e^{x_s(t)} \tag{B.17}$$

Accordingly, a convenient choice for the contour in (B.15) is the circle $w = w_s(t) = e^{i\varphi}$, with $-\pi < \varphi \leqslant \pi$. With this choice the integral in (B.15) has been calculated by Scott(14) and Ziff *et al.*(12) The outcome is

$$c_k(t) \sim k^{-5/2}[2\pi t^3 u''(x_0^s)]^{-1/2}\, w_s(t)^{-k} \qquad (k \to \infty) \tag{B.18}$$

This result is valid in both the pre- and post-gel stages. In the vicinity of the gelpoint we have

$$x_0^s(t) \sim [t_c^2 u''(0)]^{-1}(t_c - t) \qquad (t \to t_c) \tag{B.19}$$

The result (B.18) represents the so-called *universal* form of the cluster size distribution,(25,26) which is the correct form if there exists a root $x_0^s(t)$ of Eq. (B.16). There exists the possibility for nonuniversal solutions for certain classes of initial conditions(25,26); this will not be discussed here.

B.3. The Scaling Limit

Next we consider the cluster size distribution in the scaling limit, which is the limit where the average cluster size diverges: $s(t) \to \infty$ and $k \to \infty$, with the ratio $r \equiv k/s(t)$ fixed. In the scaling limit (S), $c_k(t)$ approaches a scaling form(11)

$$c_k(t) \xrightarrow{\mathrm{S}} s(t)^{-5/2}\,\varphi(r) \tag{B.20}$$

The scaling function $\varphi(r)$ is given by

$$\varphi(r) = Br^{-5/2}e^{-\delta r} \tag{B.21a}$$

where the constants B and δ are determined by the initial conditions and by the precise definition of the average cluster size. If we choose $s(t) \equiv M_3(t)/M_2(t)$, which is the choice of Ref. 12, we find that

$$B = [2\pi t_c^3 u''(0)]^{-1/2}; \qquad \delta = \tfrac{1}{2} \tag{B.21b}$$

Different choices for $s(t)$ lead to different numerical values in (B.21b).

A different but equivalent formulation of the scaling law (B.20) is obtained if we consider the generating function $(\partial f/\partial x)(x, t)$ instead of $c_k(t)$. One finds that $(\partial f/\partial x)(x, t)$ approaches a scale-invariant form in the limit $x \to 0$ and $s(t) \to \infty$ with the scaling argument $\rho = -xs(t)$ kept fixed:

$$s(t)^{-1/2}\frac{df}{\partial x}(x, t) \xrightarrow{\text{S}} h(\rho); \qquad \rho \equiv -xs(t) \tag{B.22a}$$

where the scaling function $h(\rho)$ has the form

$$h(\rho) = B\sqrt{\pi}(\delta + \rho)^{-1/2} \tag{B.22b}$$

The constants B and δ are the same as in (B.21b).

We discuss the behavior in the scaling limit of $x_0^s(t)$ and $x_0(x, t)$. These results are needed in Section 5.3. First we consider the solution $x_0^s(t)$ of Eq. (B.16). The time dependence of $s(t)$ is given, due to (B.11)–(B.14), by

$$s(t) = M_3(t)/M_2(t) \sim t_c^3 u''(0)(t_c - t)^{-2} \qquad (t \to t_c) \tag{B.23}$$

so that x_0^s in (B.19) can be expressed as a function of $s(t)$ as follows:

$$\begin{aligned} x_0^s(t) &\sim [u'(0)/u''(0)]^{1/2}\, s(t)^{-1/2} && (t \uparrow t_c) \\ x_0^s(t) &\sim -[u'(0)/u''(0)]^{1/2}\, s(t)^{-1/2} && (t \downarrow t_c) \end{aligned} \tag{B.24}$$

Next we consider the function $x_0(x, t)$ defined in (B.4b). From (B.22a) a infer that

$$f(x, t) \xrightarrow{\text{S}} M_1(t) - 2\pi^{1/2}B[(\delta + \rho)^{1/2} - \delta^{1/2}]\, s(t)^{-1/2} \tag{B.25}$$

where $M_1(t)$ can be expressed in terms of $s(t)$ due to (B.8a):

$$M_1(t) = 1 \qquad (t < t_c) \tag{B.26a}$$

$$M_1(t) \sim 1 - 2[t_c^3 u''(0)\, s(t)]^{-1/2} \qquad (t \downarrow t_c) \tag{B.26b}$$

Combination of (B.4b), (B.25), (B.26a), and (B.26b) finally shows that $x_0(x, t)$ vanishes in the scaling limit, proportional to $s(t)^{-1/2}$:

$$x_0(x, t) \xrightarrow{\text{S}} -C_{\pm}(\rho)\, s(t)^{-1/2} \tag{B.27a}$$

where the prefactor $C(\rho)$ in (B.27a) is different below and above the gelpoint:

$$\begin{aligned} C_-(\rho) &= 2\pi^{1/2}Bt_c[(\delta + \rho)^{1/2} - \delta^{1/2}] && (t \uparrow t_c) \\ C_+(\rho) &= C_-(\rho) + 2[t_c^3 u''(0)]^{-1/2} && (t \downarrow t_c) \end{aligned} \tag{B.27b}$$

In summary: both x_0^s and $x_0(x, t)$ vanish proportional to $s(t)^{-1/2}$, but the behavior of $x_0(x, t)$ is nonuniform in $\rho = -xs(t)$.

B.4. The Large-Time Limit ($t \to \infty$)

In the large-time limit we know from (B.4) that for a fixed value of x

$$x_0(x, t) \sim -t \to -\infty \qquad (t \to \infty) \tag{B.28}$$

so that $f(x, t)$ in (B.4a) is determined mainly by the first few terms in the series expansion of $u(x)$:

$$f(x, t) = c_1(0)\, e^{x_0} + 2c_2(0)\, e^{2x_0} + \cdots \qquad (t \to \infty) \tag{B.29}$$

Inversion of (B.29) and use of (B.4b) gives an expression for $x(f, t)$ as $t \to \infty$:

$$w = e^x = [f/c_1(0)]\, e^{-tf+t}\{1 - [2c_2(0)/c_1(0)^2]\, f + \cdots\} \qquad (t \to \infty) \tag{B.30}$$

Substitution of (B.30) into (B.15) and calculation of the integral gives

$$c_k(t) = [c_1(0)]^k \frac{(kt)^{k-1}}{kk!}$$
$$\times e^{-kt}\{1 + (k-1)[2c_2(0)/c_1(0)^2]\, t^{-1} + \cdots\} \qquad (t \to \infty) \tag{B.31}$$

At large times the dominant species, at least in the sol, are the monomers. Larger polymers become rare.

B.5. Monodisperse Initial Conditions

In particular, we need the results for an initially monodisperse system, i.e., $c_k(0) = \delta_{k1}$. In this case $u(x) = e^x$, so that the function $x(f, t)$ in (B.4) can be calculated explicitly

$$e^x = fe^{-tf+t} \tag{B.32}$$

This result can be used in combination with (B.15) to give an explicit expression for $c_k(t)$, namely

$$c_k(t) = (k^{k-2}/k!)\, t^{k-1} e^{-kt} \tag{B.33}$$

In this special case the phase transition occurs at $t_c = 1$. The asymptotic results (B.18), (B.20), and (B.31) can readily be verified for $c_k(t)$ in (B.33).

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