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Spatial Fluctuations in Reaction-Limited Aggregation

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A general method is used for describing reaction–diffusion systems, namely van Kampen's "method of compounding moments," to study the spatial fluctuations in reaction-limited aggregation processes. The general formalism used here and in subsequent publications is developed. Then a particular model is considered that is of special interest, since it describes the occurrence of a phase transition (gelation). The corresponding rate constants for the reaction between two clusters of size i and size j are $K_{ij} = ij$ ($i, j = 1, 2,...$). For the *diffusion constants* D_j of clusters of size j the following class of models is considered: $D_j = D$ if $1 \leqslant j \leqslant s$ and $D_j = 0$ if $j > s$. The cases $s = \infty$ and $s < \infty$ are studied separately. For the model $s = \infty$ the equal-time and the two-time correlation functions are calculated; this model *breaks down* at the gel point. The breakdown is characterized by a divergence of the density fluctuations, and is caused by the large mobility of large clusters. For all models with $s < \infty$ the density fluctuations remain finite at t_c, and the equal-time correlation functions in the pre- and in the post-gel stage are calculated. Many explicit and asymptotic results are given. From the exact solution the upper critical dimension in this gelling model is $d_c = 2$.

KEY WORDS: Spatial fluctuations; reaction–diffusion; aggregation; phase transition; gelation.

1. INTRODUCTION

Reaction–diffusion systems are particularly suited as an object of study if one is interested in the time evolution of averages (concentrations) and spatial fluctuations about these averages. The reason is that the mobility of the reactants permits a rather tractable stochastic description based on cluster expansions,(1,2) field operator representations,(3,4) or the master

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equation.$^{(5-8)}$ These methods can then be used to derive kinetic equations, from which the concentrations and correlation functions may be studied.

In this paper I apply a general method for studying reaction–diffusion systems to a model describing the irreversible aggregation of clusters. The model under consideration is of special interest, since it describes the occurrence of a nonequilibrium *phase transition* (gelation), and the spatial fluctuations can be studied in detail both before and beyond the critical time t_c.

The method for studying the fluctuations is the so-called "method of compounding moments" devised by van Kampen.$^{(5)}$ According to this method, the derivation of kinetic equations for the averages and for the fluctuations about these averages proceeds in two steps. In the first step one discretizes the space, i.e., one constructs the master equation for a *cell model*, where clusters react within each cell and jump between the cells. The kinetic equations are then derived *directly from the master equation for this cell model.* In the second step one transforms from the cell picture to a continuous formulation, replacing the cell index by the spatial coordinates **r**. The advantages of this approach over the competing functional integral approach are expounded in ref. 5. However, in *either* approach it is assumed that the clusters travel over large distances (visit many cells) before they finally react. This reveals the basic limitation of the method: I restrict consideration to aggregation processes that are *reaction limited.*

Before discussing the stochastic (master equation) approach, I consider first the macroscopic law for the average density of clusters of size k, or k-mers ($k=1, 2,\ldots$). The concentrations $c_k(\mathbf{r}, t)$ of clusters of size k at the position **r** can be described by a set of *deterministic*, coupled reaction–diffusion equations of the form

$$\begin{aligned}\frac{\partial}{\partial t} c_k(\mathbf{r}, t) = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i(\mathbf{r}, t)\, c_j(\mathbf{r}, t) - c_k(\mathbf{r}, t) \sum_{j=1}^{\infty} K_{kj} c_j(\mathbf{r}, t)\\ + D_k \Delta c_k(\mathbf{r}, t) \qquad (k=1, 2,\ldots) \qquad (1.1)\end{aligned}$$

where $\Delta = \partial^2/\partial \mathbf{r}^2$ is the diffusion operator, and K_{ij} and D_k are the reaction and diffusion constants, respectively. The various terms on the right in (1.1) represent, respectively, the formation of k-mers out of i- and j-mers (with $i+j=k$), the loss of k-mers due to reactions with other polymers, and the change in $c_k(\mathbf{r}, t)$ due to diffusion. Clearly, fluctuations are neglected in (1.1). Furthermore, in Eq. (1.1) only reactions between clusters of *finite* size (*sol* particles) are taken into account. If the system contains also an *infinite* cluster (or *gel*), then Eq. (1.1) has to be supplemented with a term describing the reactivity of the gel.

The master equation is constructed as follows. We start from the usual cell model, where the total volume V of the system is subdivided into cells of size v. The cells should be so small that they can be considered homogeneous. In this case the possible states of the system are fully characterized by the vector $\mathbf{m}=\{m_{k\lambda}\}$, where $m_{k\lambda}$ gives the number of k-mers in cell λ. The probability $P(\mathbf{m}, t)$ that the system is in state $\mathbf{m}$ at time t changes due to two effects: the *reactions*, taking place within the cell, and the *diffusion*, which is modeled by jumps between the cells. Accordingly, the master equation for $P(\mathbf{m}, t)$ contains *two* terms:

$$\dot{P}(\mathbf{m}, t)=T_{\mathrm{R}}(\mathbf{m}, t)+T_{\mathrm{D}}(\mathbf{m}, t) \tag{1.2}$$

where T_{R} and T_{D} represent the reaction and diffusion processes, respectively.

The explicit form of the reaction part in (1.2) is given by

$$\begin{aligned} T_{\mathrm{R}}(\mathbf{m}, t)=(2v)^{-1} \sum_{i,j,\lambda} K_{ij}\big[&(m_{i\lambda}+1+\delta_{ij})(m_{j\lambda}+1)\, P(\mathbf{m}_{\mathrm{R}}, t) \\ &- m_{i\lambda}(m_{j\lambda}-\delta_{ij})\, P(\mathbf{m}, t)\big] \end{aligned} \tag{1.3a}$$

where the state $\mathbf{m}_{\mathrm{R}}$ differs from $\mathbf{m}$ only in the numbers of i-mers, j-mers, and $(i+j)$-mers in cell λ:

$$\mathbf{m}_{\mathrm{R}}=(\ldots, m_{i\lambda}+1+\delta_{ij},\ldots, m_{j\lambda}+1+\delta_{ij},\ldots, m_{i+j\lambda}-1,\ldots) \tag{1.3b}$$

Thus T_{R} contains a gain and a loss term, corresponding to the first and second terms on the right in (1.3a). The gain term represents jumps toward the state $\mathbf{m}$ from a state with an i- and a j-mer more in cell λ and an $(i+j)$-mer less. The loss term represents jumps out of state $\mathbf{m}$.

The contribution T_{D} due to diffusion takes the form

$$T_{\mathrm{D}}(\mathbf{m}, t)=\sum_{\lambda,\mu,l} w_{\mu\lambda}^{(l)}\big[(m_{l\lambda}+1)\, P(\mathbf{m}_{\mathrm{D}}, t)-m_{l\lambda} P(\mathbf{m}, t)\big] \tag{1.4a}$$

where

$$\mathbf{m}_{\mathrm{D}} \equiv (\ldots, m_{l\lambda}+1,\ldots, m_{l\mu}-1,\ldots) \tag{1.4b}$$

and $w_{\mu\lambda}^{(l)}$ gives the transition rate for jumps by l-mers from cell λ to cell μ. There is again a gain and a loss term, corresponding to the first and second terms on the right in (1.4a). In this case the gain term describes jumps toward $\mathbf{m}$ from states with an l-mer in cell λ more and an l-mer in cell μ less.

The relation between the stochastic equation (1.2) and the deterministic equation (1.1) is that the average k-mer density $\langle m_{k\lambda}\rangle/v$ reduces to $c_k(\mathbf{r}, t)$ if the diffusion (or jump) constants are *large*. In this case one can transform from the cell picture to a continuum formulation, replacing $m_{k\lambda}/v$ by the density $u_k(\mathbf{r}, t)$ and $w_{\mu\lambda}^{(k)}$ by D_k. As a result, one finds that the average density $\langle u_k(\mathbf{r}, t)\rangle$ satisfies the macroscopic law (1.1).

A conserved quantity in (1.2), and also in (1.1), is the total number of monomeric units (or total mass) in the system. Hence, if the total mass is denoted by M, one has the following restriction on the possible states $\mathbf{m}$ in (1.2):

$$\sum_{\lambda} \sum_{k=1}^{M} k m_{k\lambda} = M \tag{1.5}$$

By convention I choose the unit of volume such that $M = V$, i.e., I set the mass density equal to unity. Next consider Eq. (1.1). The situation here is complicated by the fact that for some choices of the rate constants K_{ij}, Eq. (1.1) predicts a phase transition at a finite time t_c, where an infinite cluster, or gel, is formed. Hence the total mass is the sum of the sol and the gel mass, and only the sum of both is conserved:

$$V^{-1} \int d\mathbf{r} \left[\sum_k k c_k(\mathbf{r}, t) + g(\mathbf{r}, t) \right] = 1 \qquad (t > t_c) \tag{1.6}$$

Here $g(\mathbf{r}, t)$ represents the mass density of the gel. The constant on the right-hand side of (1.6) is equal to unity, due to the choice $M = V$.

In this paper I consider one particular choice for the reaction rates K_{ij} in (1.3), or (1.1), that leads to a gelation transition within a finite time:

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

The model (1.7) is a stylized version of the classical polymerization models $\mathrm{RA_f}$ and $\mathrm{A_fRB_g}$ of Flory and Stockmayer,(9-11) which describe the growth of branched polymers. Equation (1.7) implies that the reactivity of a cluster is chosen proportional to its *mass*. Hence, if a gel also occurs, then the reactivity of the gel is proportional to $g(\mathbf{r}, t)$. Accordingly, the macroscopic law (1.1) assumes the form

$$\begin{aligned} \frac{\partial}{\partial t} c_k(\mathbf{r}, t) = {} & \frac{1}{2} \sum_{i+j=k} ij c_i(\mathbf{r}, t)\, c_j(\mathbf{r}, t) - k c_k(\mathbf{r}, t) \left[\sum_{j=1}^{\infty} j c_j(\mathbf{r}, t) + g(\mathbf{r}, t) \right] \\ & + D_k \Delta c_k(\mathbf{r}, t) \qquad (k = 1, 2, \ldots) \end{aligned} \tag{1.8a}$$

The loss term on the right in (1.8a) shows that k-mers may react with j-mers ($j = 1, 2, \ldots$) and with the gel. The time dependence of $g(\mathbf{r}, t)$ in (1.8a) is determined by

$$\frac{\partial}{\partial t} g(\mathbf{r}, t) = g(\mathbf{r}, t) \sum_{k=1}^{\infty} k^2 c_k(\mathbf{r}, t) \tag{1.8b}$$

Equation (1.8b) simply states that reactions between k-mers and the gel occur at a rate $kc_k g$, each reaction adding k units to the gel. Throughout this paper it is assumed that the gel network is immobile, i.e., that diffusion of the gel does not occur.

The exact solution of Eqs., (1.8a), (1.8b) with a *general* initial condition $c_k(\mathbf{r}, 0)$ is not known. This is unfortunate, since we are interested in the spatial fluctuations about $c_k(\mathbf{r}, t)$, and the fluctuations can be calculated only *after* the macroscopic law (1.8) has been solved. However, Eq. (1.8) can be solved for one important *special case*, namely if the initial distribution is spatially uniform:

$$c_k(\mathbf{r}, 0) = c_k(0); \qquad g(\mathbf{r}, 0) = g(0) \tag{1.9a}$$

In this case the solution $c_k(\mathbf{r}, t)$ of (1.8) is also independent of $\mathbf{r}$, i.e.,

$$c_k(\mathbf{r}, t) = c_k(t); \qquad g(\mathbf{r}, t) = g(t) \tag{1.9b}$$

where $c_k(t)$ and $g(t)$ satisfy the coupled chemical rate equations

$$\dot{c}_k(t) = \frac{1}{2} \sum_{i+j=k} ij c_i(t)\, c_j(t) - k c_k(t) \qquad (k = 1, 2,...) \tag{1.10a}$$

$$\dot{g}(t) = g(t)\, M_2(t) \tag{1.10b}$$

In the derivation of (1.10) I used the mass conservation law (1.6) in spatially uniform systems, i.e.,

$$\sum_{k=1}^{\infty} k c_k(t) + g(t) = 1 \tag{1.11}$$

and introduced the *moments* $M_n(t)$ of $c_k(t)$, which are defined as

$$M_n(t) \equiv \sum_{k=1}^{\infty} k^n c_k(t) \tag{1.12}$$

In the bulk of this paper I consider spatially uniform systems, as in (1.9a). The more general case, where the initial distribution contains statistical fluctuations, is discussed in Section 5.

The chemical rate equation (1.10) is a special case of *Smoluchowski's coagulation equation*,⁽¹²⁻¹⁴⁾ corresponding to the choice (1.7) for the rate constants K_{ij}. Equation (1.10) has been solved for a general initial distribution $c_k(0)$ by Scott⁽¹⁵⁾ and, more recently, by Ziff *et al.*⁽¹⁶⁾ A summary of the properties of $c_k(t)$ can be found in Appendix B of ref. 17. Here I mention only the results for *monodisperse initial conditions*, $c_k(0) = \delta_{k1}$, since in this paper most attention is paid to this case. The cluster size distribution in the sol is, for all $t \geqslant 0$, given by

$$c_k(t) = k^{k-2}(te^{-t})^k/k!\,t \qquad (k = 1, 2,...) \tag{1.13}$$

The concentration $g(t)$ of the gel can now be calculated from (1.11). In the pre-gel stage ($t < t_c = 1$) all mass is contained in the sol: $\sum_{k=1}^{\infty} kc_k(t) = 1$, so that $g(t)$ vanishes. In the post-gel stage ($t > 1$) it follows from (1.13) that $g(t) = (t - t^*)/t$, where $t^*(t)$ is the root of the equation $t^* \exp(-t^*) = t \exp(-t)$ in the interval $0 < t^* < 1$. This implies that $g(t)$ increases linearly just above t_c: $g(t) \sim 2(t-1)$ as $t \downarrow 1$. For $t \to \infty$ one finds that $g(t) \to 1$, implying that at large times all mass is contained in the gel. An important characteristic of the gel point is the divergence$^{(11)}$ at t_c of the moments $M_n(t)$, with $n \geqslant 2$. For instance, for $n = 2$ one finds that $M_2(t) = (1-t)^{-1}$ if $t < 1$, and $M_2(t) \sim (t-1)^{-1}$ if $t \downarrow 1$.

To my knowledge, the solution of the master equation (1.2)–(1.4) with K_{ij} as in (1.7) is not known for any initial distribution. Master equations of the form (1.2) have been written down, e.g., by Elderfield$^{(8)}$ and Burschka,$^{(18)}$ but these authors are concerned mainly with the macroscopic law$^{(8)}$ or with the fundamental problems in the description of reaction–diffusion systems.$^{(18)}$ Much more is known about the simpler problem of the master equation for a single, isolated cell. This master equation is obtained from (1.2) if one forbids the jumps between cells and focuses on one of the cells λ. The master equation for the single cell has been solved exactly by Lushnikov,$^{(19)}$ who calculates also the *average number* of k-mers $\langle m_k(t) \rangle$. The *fluctuations* in the single cell have been studied extensively by van Dongen and Ernst.$^{(17)}$ The present paper extends the results of ref. 17 for spatially homogeneous systems to the combined problem of reaction and diffusion.

The quantities of main interest in this paper are the *equal-time* and *two-time* correlation functions of the concentrations of k- and l-mers. In the continuous formulation, where $m_{k\lambda}$ is replaced by the k-mer density $u_k(\mathbf{r}) = m_{k\lambda}/v$, the two-time correlation functions are defined as

$$\langle\!\langle u_k(\mathbf{r}_1, t_1)\, u_l(\mathbf{r}_2, t_2) \rangle\!\rangle \equiv \langle \Delta u_k(\mathbf{r}_1, t_1)\, \Delta u_l(\mathbf{r}_2, t_2) \rangle \tag{1.14}$$

where $\Delta u_k(\mathbf{r}, t) \equiv u_k(\mathbf{r}, t) - \langle u_k(\mathbf{r}, t) \rangle$. The equal-time correlation functions (or covariances) are obtained from (1.14) by setting $t_2 = t_1$.

The organization of this paper is as follows. Section 2 presents the details of the method and derives the basic equations to be used in subsequent sections. Sections 3 and 4 are devoted to *two exactly soluble models*. The model to be considered in Section 3 corresponds to diffusion constants D_k independent of the cluster size:

$$D_k = D \qquad (k = 1, 2,...) \tag{1.15}$$

For this model the equal-time and two-time correlation functions can be calculated exactly, but *only* in the pre-gel stage ($t_1, t_2 < t_c$). It is shown that, for D_k as in (1.15), the density fluctuations diverge at the gel point, due to the large mobility of large clusters. Hence one needs a different model, where large clusters are less mobile, to study the fluctuations in the post-gel stage. The simplest choice is

$$D_k = D \quad (k = 1,..., s); \qquad D_k = 0 \quad (k > s) \tag{1.16}$$

This second model is the subject of Section 4. Although I have only been able to calculate the equal-time correlation functions, the results show many interesting properties of the fluctuations in the presence of a gel. For example, the upper critical dimension in this gelling model is $d_c = 2$. Finally, Section 5 discusses and summarizes the results. The body of this paper is restricted to monodisperse initial conditions. Some results for the model (1.15) with a general initial condition are given in the Appendix.

2. METHOD AND BASIC EQUATIONS

In this section kinetic equations are derived for the concentrations of sol and gel clusters and for the equal-time and two-time correlation functions. The basic assumption underlying the derivation is that the coagulation process is *reaction limited.* In this case one can apply the Ω-expansion(5) to the reaction part in (1.3). Moreover, one can transform from the cell picture to a continuum formulation, replacing the cell index α by the spatial coordinates **r**.

One starts with the observation that the master equation (1.2) is *not* the most appropriate starting point to study the fluctuations in *gelling systems.* The reason has been discussed in ref. 17: to apply the Ω-expansion to the reaction part of (1.2), one has to be able to distinguish between the sol and the gel. However, at the level of the master equation (1.2), each cell represents a *finite* system, and in finite systems the distinction between sol and gel clusters is rather vague. More precisely: in finite systems such as (1.2) the "gel" is not properly defined.

For the special case of the model $K_{ij} = ij$, this problem may be solved as follows. Consider the jump rates $w_{\mu\lambda}^{(l)}$ in (1.3) or, equivalently, the diffusion constants D_k in (1.8). Eventually, it is our object to construct a model where the sol clusters are *mobile* and the gel is *immobile.* For the diffusion constants this implies that we seek a model with

$$D_k > 0 \quad (k = 1, 2,...); \qquad D_0 = 0 \tag{2.1}$$

Here D_0 is the diffusion constant of the gel. The crucial observation is that (2.1) corresponds to the limit $r \to \infty$ of a *different* model, where only clusters of size $k \leqslant r$ can diffuse and all larger clusters are immobile:

$$D_k > 0 \quad (k = 1,..., r); \qquad D_k = 0 \quad (k > r) \tag{2.2}$$

For models of the form (2.2) there occurs an essential simplification, namely that the system can be described in terms of only $r+1$ reactants. These $r+1$ reactants are the k-mers, with $1 \leqslant k \leqslant r$, and the clusters larger than r. For nonspatial systems, this observation was made already in ref. 17.

The point here is that it is possible, at least for the model $K_{ij} = ij$, to construct a master equation for the *marginal probability distribution* that the system is in state $\{\mathbf{m}_\lambda^{(r)}\}$. The vector $\mathbf{m}_\lambda^{(r)}$ is defined as

$$\mathbf{m}_\lambda^{(r)} \equiv (m_{1\lambda}, m_{2\lambda},..., m_{r\lambda}; m_{0\lambda}) \tag{2.3}$$

where $m_{k\lambda}$ $(k = 1,..., r)$ is the number of k-mers in cell λ, and $m_{0\lambda} \equiv \sum_{k>r} km_{k\lambda}$ is the mass contained in clusters larger than r. The master equation in terms of the states $\mathbf{m} \equiv \{\mathbf{m}_\lambda^{(r)}\}$ has the same form as in (1.2),

$$\dot{\mathbf{P}}_r(\mathbf{m}, t) = T_\mathrm{R}(\mathbf{m}, t) + T_\mathrm{D}(\mathbf{m}, t) \tag{2.4}$$

but the reaction and diffusion terms are slightly modified. The diffusion part of (2.4) is relatively simple. It has the same form as in (1.4), but now with zero jump rates for clusters larger than r:

$$T_\mathrm{D}(\mathbf{m}, t) = \sum_{\lambda,\mu} \sum_{l=1}^{r} w_{\mu\lambda}^{(l)}[(m_{l\lambda} + 1)\, P(\mathbf{m}_\mathrm{D}, t) - m_{l\lambda} P(\mathbf{m}, t)] \tag{2.5}$$

where $\mathbf{m}_\mathrm{D}$ differs from $\mathbf{m}$ only in the numbers of l-mers in cell λ and in cell μ, as in (1.4b).

Equation (2.5) describes the diffusion of l-mers (with $l = 1,..., r$) from cell λ to cell μ, similarly as in (1.4). The reaction part in (2.4) is more complicated, and will be discussed next.

Clusters in cell λ are involved in *three types of reactions*:

(i) Reactions between i- and j-mers with both $i \leqslant r$ and $j \leqslant r$. The transition rates for this process are the same as in (1.3), but now with $i, j \leqslant r$.

(ii) Reactions between clusters with $i \leqslant r$ and $j > r$. The corresponding transition rate (summed over all possible j) is $v^{-1} i m_{i\lambda} m_{0\lambda}$.

(iii) Reactions with $i > r$ and $j > r$. Such reactions do not change the state $\mathbf{m}_\lambda^{(r)}$ and hence do not contribute to (2.4).

Note that the transition rates in processes (i) and (ii) depend *only* on the numbers $m_{k\lambda}$ $(k=0, 1, \ldots, r)$ and *not* on the details of the cluster size distribution for $k>r$. As a consequence, one could write down an explicit expression for $T_R(\mathbf{m}, t)$, as in (1.3), but for the present purposes it is more convenient to cast T_R in the compact form

$$T_R(\mathbf{m}, t)=\sum_{\lambda}\left\{\frac{1}{2}\sum_{i,j=1}^{r} K_{ij}\,\Delta_{ij\lambda}[v^{-1}m_{i\lambda}(m_{j\lambda}-\delta_{ij})\,P_r]\right.$$
$$\left.+\sum_{i=1}^{r} i\,\Delta_{i\lambda}(v^{-1}m_{i\lambda}m_{0\lambda}P_r)\right\} \tag{2.6}$$

where the difference operators $\Delta_{ij\lambda}$ and $\Delta_{i\lambda}$ are defined, for arbitrary functions $f(\mathbf{m})$, as

$$\Delta_{ij\lambda}f(\mathbf{m})=f(\{m_{k\nu}+\delta_{\lambda\nu}(\delta_{ik}+\delta_{jk}-\delta_{i+j,k}),$$
$$m_{0\nu}-(i+j)\,\delta_{\lambda\nu}\eta_{i+j-r}\})-f(\mathbf{m}) \tag{2.7a}$$

$$\Delta_{i\lambda}f(\mathbf{m})=f(\{m_{k\nu}+\delta_{\lambda\nu}\delta_{ik}, m_{0\nu}-i\delta_{\lambda\nu}\})-f(\mathbf{m}) \tag{2.7b}$$

In (2.7a) I introduced a step function η_x:

$$\eta_x=0 \quad (x\leqslant 0); \qquad \eta_x=1 \quad (x>0) \tag{2.8}$$

The interpretation of Eqs. (2.6) and (2.7) is as follows. The terms in (2.6) containing $\Delta_{ij\lambda}$ describe reactions of the form (i) with $i, j\leqslant r$. There is a gain term and a loss term, corresponding to the first and the second term, respectively, on the rhs of (2.7a). The loss term corresponds to jumps out of the state **m**. The gain term represents jumps toward **m** from states with an i-mer and a j-mer more and an $(i+j)$-mer less. The step function shows that one must distinguish the possibilities $i+j\leqslant r$ and $i+j>r$. Similarly, the forms containing $\Delta_{i\lambda}$ describe reactions of the form (ii).

I now proceed as follows. From the structure of the master equation (2.4), it is clear that the kinetic equations, to be derived below, consist of two parts: a reaction part, due to T_R, and a diffusion part, due to T_D. These contributions will be discussed separately: I consider first the contributions due to reactions (Section 2.1), and then the diffusion terms (Section 2.2). In Section 2.3 I collect results and discuss the transition to a continuous description. Finally, Section 2.4 is devoted to the special case where the initial state of the system (at $t=0$) is spatially uniform. For such systems the kinetic equations are comparatively simple.

2.1. Contributions Due to Reactions

Let us start from the master equation (2.4) and consider only the reaction part T_R. The contributions, due to T_R, to the kinetic equations for the averages, the covariances, and the correlation functions will be discussed in this order.

The contribution due to reactions (subscript R) to the rate equation for $\langle m_{k\alpha} \rangle$ $(k=0, 1,..., r)$ may be obtained by multiplying the master equation (2.4) with $m_{k\alpha}$ and summing over all possible values of **m**. The result is, for $k=1,..., r$,

$$\frac{\partial}{\partial t} \langle m_{k\alpha} \rangle_R = -(2v)^{-1} \sum_{i,j=1}^{r} K_{ij}(\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \langle m_{i\alpha}(m_{j\alpha} - \delta_{ij}) \rangle \\ - v^{-1} k \langle m_{k\alpha} m_{0\alpha} \rangle \tag{2.9a}$$

For $k=0$ one finds that

$$\frac{\partial}{\partial t} \langle m_{0\alpha} \rangle_R = (2v)^{-1} \sum_{i,j=1}^{r} K_{ij}(i+j)\, \eta_{i+j-r} \langle m_{i\alpha}(m_{j\alpha} - \delta_{ij}) \rangle \\ + v^{-1} \sum_{i=1}^{r} i^2 \langle m_{i\alpha} m_{0\alpha} \rangle \tag{2.9b}$$

The only nonvanishing contribution to the right-hand side of Eqs. (2.9a), (2.9b) comes from the term in (2.6) corresponding to cell α. Note that Eq. (2.9) is *not* a closed equation for $\langle m_{k\alpha} \rangle$, due to the occurrence of the second moment $\langle m_{i\alpha} m_{j\alpha} \rangle$ on the right-hand side.

An approximate, closed equation for $\langle m_{k\alpha} \rangle$ may be obtained with the use of the *Ω-expansion.*(5,17) The basic idea[2] of the Ω-expansion is that the fluctuations in *large* cells are *small*, of relative order $v^{-1/2}$. In this case the occupation numbers $m_{k\alpha}$ can be split into two parts, a macroscopic part $\langle m_{k\alpha} \rangle$ and a fluctuating part $\Delta m_{k\alpha}$,

$$m_{k\alpha} = \langle m_{k\alpha} \rangle + \Delta m_{k\alpha} \qquad (k=0, 1,..., r) \tag{2.10a}$$

where $\langle m_{k\alpha} \rangle$ is of the order of v, and $\Delta m_{k\alpha}$ of the order of $v^{1/2}$. Consequently, the second moments in (2.9) can be expanded in powers of v as follows

$$\langle m_{i\alpha} m_{j\alpha} \rangle = \langle m_{i\alpha} \rangle \langle m_{j\alpha} \rangle + \langle \Delta m_{i\alpha} \, \Delta m_{j\alpha} \rangle \\ = \langle m_{i\alpha} \rangle \langle m_{j\alpha} \rangle + O(v) \qquad (v \gg 1) \tag{2.10b}$$

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[2] Actually, to make the Ω-expansion *systematic*, more sophisticated arguments are required,(5) but these refinements are of no need here.

The correction term on the right in (2.10) is negligibly small, of relative order v^{-1}, if the cell size v is large. Thus, one finds that the contribution to $\partial\langle m_{k\alpha}\rangle/\partial t$ due to reactions is given by

$$\begin{aligned}\frac{\partial}{\partial t}\langle m_{k\alpha}\rangle_{\mathrm{R}} &= -(2v)^{-1}\sum_{i,j=1}^{r} K_{ij}(\delta_{ik}+\delta_{jk}-\delta_{i+j,k})\langle m_{i\alpha}\rangle\langle m_{j\alpha}\rangle \\ &\quad - v^{-1}k\langle m_{k\alpha}\rangle\langle m_{0\alpha}\rangle \qquad (1\leqslant k\leqslant r) \qquad (2.11\mathrm{a})\\ \frac{\partial}{\partial t}\langle m_{0\alpha}\rangle_{\mathrm{R}} &= (2v)^{-1}\sum_{i,j=1}^{r} K_{ij}(i+j)\,\eta_{i+j-r}\langle m_{i\alpha}\rangle\langle m_{j\alpha}\rangle \\ &\quad + v^{-1}\sum_{i=1}^{r} i^2\langle m_{i\alpha}\rangle\langle m_{0\alpha}\rangle \qquad (2.11\mathrm{b})\end{aligned}$$

provided that the cell size v is large.

Thus, the cell size v should simultaneously satisfy two conditions. On one hand, the cells must be *large* (i.e., contain many clusters) in order that the Ω-expansion can be applied. On the other hand, the cells should be *small* compared to the average volume traversed by a cluster during its lifetime, in order that the mean-field assumption within each cell is justified. Clearly these conditions can both be fulfilled only if clusters diffuse over large distances and collide many times before they finally react. This requirement need not be unrealistic. For instance, Flory$^{(9)}$ states that in condensation polymerization generally "no more than about one bimolecular collision in 10^{13} between reactants is fruitful."

Along similar lines as in (2.11), one may derive an equation for the covariances $\langle\!\langle m_{k\alpha}m_{l\beta}\rangle\!\rangle$, which are defined as

$$\langle\!\langle m_{k\alpha}m_{l\beta}\rangle\!\rangle \equiv \langle \Delta m_{k\alpha}\,\Delta m_{l\beta}\rangle \qquad (k, l=0, 1,..., r) \qquad (2.12\mathrm{a})$$

However, the resulting kinetic equations are much simpler if one considers, instead of $\langle\!\langle m_{k\alpha}m_{l\beta}\rangle\!\rangle$, a new quantity $[m_{k\alpha}m_{l\beta}\rangle\!\rangle$ that differs from the covariances only on the diagonal, where $k=l$ and $\alpha=\beta$:

$$\left.\begin{aligned}[m_{k\alpha}m_{l\beta}\rangle\!\rangle &\equiv \langle\!\langle m_{k\alpha}m_{l\beta}\rangle\!\rangle - \delta_{kl}\delta_{\alpha\beta}\langle m_{k\alpha}\rangle \qquad (1\leqslant k, l\leqslant r)\\ &\equiv \langle\!\langle m_{k\alpha}m_{l\beta}\rangle\!\rangle \qquad (k=0 \text{ or } l=0)\end{aligned}\right. \qquad (2.12\mathrm{b})$$

Note that $[m_{k\alpha}m_{l\beta}\rangle\!\rangle$, with $0\leqslant k,\ l\leqslant r$, is a *mixed cumulant*: it is a factorial cumulant$^{(5)}$ only for $1\leqslant k,\ l\leqslant r$.

To obtain an equation for $[m_{k\alpha}m_{l\beta}\rangle\!\rangle$, it is convenient to derive an equation for the second moment $\langle m_{k\alpha}m_{l\beta}\rangle$ first. Subtraction of the equations for $\langle m_{k\alpha}\rangle(\partial/\partial t)\langle m_{l\beta}\rangle_{\mathrm{R}}$, $\langle m_{l\beta}\rangle(\partial/\partial t)\langle m_{k\alpha}\rangle_{\mathrm{R}}$, and (if $1\leqslant k\leqslant r$) $\delta_{kl}\delta_{\alpha\beta}(\partial/\partial t)\langle m_{k\alpha}\rangle_{\mathrm{R}}$ then yields the desired equation for $[m_{k\alpha}m_{l\beta}\rangle\!\rangle$. This equation is *not* closed: the right-hand side typically contains factors of the form $\langle m_{i\alpha} m_{j\alpha} \Delta m_{l\beta} \rangle$. An approximate, closed equation, valid for large cells, may be obtained with the use of the Ω-expansion. The arguments are the same as in (2.10). The result is

$$\frac{\partial}{\partial t}[m_{k\alpha} m_{l\beta}\rangle\rangle_{\mathrm{R}} = \sum_{j=0}^{r} \{A_{kj}^{(\alpha)}(t)[m_{j\alpha} m_{l\beta}\rangle\rangle + A_{lj}^{(\beta)}(t)[m_{k\alpha} m_{j\beta}\rangle\rangle\}$$

$$+ v\delta_{\alpha\beta} Q_{kl}^{(\alpha)}(t) + O(v^{1/2}) \qquad (v \gg 1) \tag{2.13}$$

The matrix $A_{kj}^{(\alpha)}(t)$ in (2.13) is given by

$$A_{kj}^{(\alpha)}(t) = -v^{-1} \sum_{i=1}^{r} K_{ij}(\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \langle m_{i\alpha} \rangle$$

$$- v^{-1} k \delta_{kj} \langle m_{0\alpha} \rangle \qquad (1 \leqslant k, j \leqslant r) \tag{2.14a}$$

$$A_{0j}^{(\alpha)}(t) = v^{-1} \sum_{i=1}^{r} K_{ij}(i+j)\, \eta_{i+j-r} \langle m_{i\alpha} \rangle$$

$$+ v^{-1} j^2 \langle m_{0\alpha} \rangle \qquad (1 \leqslant j \leqslant r) \tag{2.14b}$$

$$A_{k0}^{(\alpha)}(t) = -v^{-1} k \langle m_{k\alpha} \rangle \qquad (1 \leqslant k \leqslant r) \tag{2.14c}$$

$$A_{00}^{(\alpha)}(t) = v^{-1} \sum_{i=1}^{r} i^2 \langle m_{i\alpha} \rangle \tag{2.14d}$$

The inhomogeneity $Q_{kl}^{(\alpha)}(t)$ has the form

$$Q_{kl}^{(\alpha)}(t) = -v^{-2} kl \langle m_{k\alpha} \rangle \langle m_{l\alpha} \rangle \qquad (1 \leqslant k, l \leqslant r) \tag{2.15a}$$

$$Q_{0k}^{(\alpha)}(t) = Q_{k0}^{(\alpha)}(t) = 0 \qquad (1 \leqslant k \leqslant r) \tag{2.15b}$$

$$Q_{00}^{(\alpha)}(t) = \frac{1}{2} v^{-2} \sum_{i,j=1}^{r} K_{ij}(i+j)^2\, \eta_{i+j-r} \langle m_{i\alpha} \rangle \langle m_{j\alpha} \rangle$$

$$+ v^{-2} \langle m_{0\alpha} \rangle \sum_{i=1}^{r} i^3 \langle m_{i\alpha} \rangle \tag{2.15c}$$

Note that the correction term in (2.13) can be neglected if v is large.

Finally, consider the two-time *correlation functions* $\kappa_{lk}^{\beta\alpha}(t_2, t_1)$, which are defined as

$$\kappa_{lk}^{\beta\alpha}(t_2, t_1) \equiv \langle\langle m_{k\alpha}(t_1)\, m_{l\beta}(t_2) \rangle\rangle$$

$$= \langle \Delta m_{k\alpha}(t_1)\, \Delta m_{l\beta}(t_2) \rangle \qquad (t_2 \geqslant t_1 \geqslant 0) \tag{2.16}$$

The correlation functions show how the fluctuation $\Delta m_{l\beta}$ at time t_2 in cell β is influenced by the fluctuation $\Delta m_{k\alpha}$ at the earlier time t_1 in cell α. Throughout, I choose $t_2 \geqslant t_1 \geqslant 0$.

The calculation of the correlation functions consists of two steps. The *first step* is the calculation of the conditional average

$$\overline{\Delta m_{l\beta}}(t) \equiv \langle \Delta m_{l\beta}(t) \,|\, \mathbf{m}(t_1) \rangle \tag{2.17}$$

for a given value of the fluctuations at time t_1. It follows immediately from (2.10a), in combination with (2.11), that $\overline{\Delta m_{l\beta}}$ satisfies the linearization of Eq. (2.11), i.e.,

$$\left(\frac{\partial}{\partial t}\overline{\Delta m_{l\beta}}(t)\right)_{\mathrm{R}} = \sum_{j=0}^{r} A_{lj}^{(\beta)}(t)\,\overline{\Delta m_{j\beta}}(t) + O(1) \qquad (v \gg 1) \tag{2.18}$$

where $A_{lj}^{(\beta)}(t)$ is given in (2.14). The initial condition for Eq. (2.18) is $\overline{\Delta m_{l\beta}}(t_1) = \Delta m_{l\beta}(t_1)$. The *second step* in the calculation of the correlation functions is to multiply $\overline{\Delta m_{l\beta}}(t)$ with the initial fluctuation $\Delta m_{k\alpha}(t_1)$ and to average over all possible values of $\mathbf{m}(t_1)$. As a consequence, one finds that the correlation functions $\kappa_{lk}^{\beta\alpha}(t, t_1)$ also satisfy an equation of the form (2.18), i.e.,

$$\left(\frac{\partial}{\partial t}\kappa_{lk}^{\beta\alpha}(t, t_1)\right)_{\mathrm{R}} = \sum_{j=0}^{r} A_{lj}^{(\beta)}(t)\,\kappa_{jk}^{\beta\alpha}(t, t_1) + O(1) \qquad (v \gg 1) \tag{2.19}$$

in this case with the initial condition

$$\kappa_{lk}^{\beta\alpha}(t_1, t_1) = \langle\!\langle m_{k\alpha}(t_1)\, m_{l\beta}(t_1) \rangle\!\rangle$$

2.2. Contributions Due to Diffusion

Diffusion (subscript D) is described by the second term, T_{D}, in the master equation (2.4). Recall that only clusters of size $k \leqslant r$ can diffuse: $w_{\mu\lambda}^{(0)} = 0$. It is an elementary excercise (ref. 5, Section VII.6) to verify that the contribution of the diffusion part T_{D} to $(\partial/\partial t)\langle m_{k\alpha} \rangle$ is exactly given by

$$\frac{\partial}{\partial t}\langle m_{k\alpha} \rangle_{\mathrm{D}} = \sum_{\lambda} W_{\alpha\lambda}^{(k)} \langle m_{k\lambda} \rangle \tag{2.20a}$$

where the matrix $W_{\alpha\lambda}^{(k)}$ is related to the hopping probabilities $w_{\alpha\lambda}^{(k)}$ in T_{D} as

$$W_{\alpha\lambda}^{(k)} = w_{\alpha\lambda}^{(k)} - \delta_{\alpha\lambda} \sum_{\beta} w_{\beta\alpha}^{(k)} \tag{2.20b}$$

Similarly, one can show (ref. 5, Section VII.6) that diffusion yields the following contribution to the rate equation for the cumulants $[m_{k\alpha}m_{l\beta}\rangle\!\rangle$:

$$\frac{\partial}{\partial t}[m_{k\alpha}m_{l\beta}\rangle\!\rangle_{\mathrm{D}}=\sum_{\lambda}W^{(l)}_{\beta\lambda}[m_{k\alpha}m_{l\lambda}\rangle\!\rangle+\sum_{\lambda}W^{(k)}_{\alpha\lambda}[m_{k\lambda}m_{l\beta}\rangle\!\rangle \tag{2.21}$$

Finally, from (2.20a) it follows directly that the conditional averages $\overline{\Delta m_{l\beta}}(t)$, and hence also the correlation functions $\kappa^{\beta\alpha}_{lk}(t,t_1)$, satisfy an equation of the form (2.20a), i.e.,

$$\left(\frac{\partial}{\partial t}\kappa^{\beta\alpha}_{lk}(t,t_1)\right)_{\mathrm{D}}=v\sum_{\lambda}W^{(l)}_{\beta\lambda}\kappa^{\lambda\alpha}_{lk}(t,t_1) \tag{2.22}$$

The kinetic equations for the averages and correlation functions are now found by "compounding the moments,"(5) i.e., by combining the diffusion terms (2.20a), (2.21), and (2.22) with the reaction terms (2.11), (2.13), and (2.19).

2.3. The Continuum Formulation

The formulation used above in terms of a discretized space subdivided into cells of size v, is somewhat unsatisfactory: in real, continuous systems there is no basis for the unique position of the "cell." Hence, the kinetic equations should not depend on the physically irrelevant parameter v.

For this reason I transform from the cell picture to a continuous formulation, replacing the cell index α by the spatial coordinate $\mathbf{r}$ and the occupation numbers $m_{k\alpha}$ by the k-mer density $u_k(\mathbf{r})$. The transformation may be summarized as

$$m_{k\alpha}/v\to u_k(\mathbf{r})\qquad (k=0,1,\ldots,r) \tag{2.23a}$$

$$v\sum_{\lambda}\to\int d\mathbf{r} \tag{2.23b}$$

$$\delta_{\alpha\lambda}/v\to\delta(\mathbf{r}-\mathbf{r}') \tag{2.23c}$$

$$\sum_{\lambda}W^{(k)}_{\alpha\lambda}\to\int d\mathbf{r}'\;W_k(\mathbf{r}\,|\,\mathbf{r}') \tag{2.23d}$$

The integrals in (2.23b), (2.23d) are over all space. In (2.23d) I have replaced the hopping rates $W^{(k)}_{\alpha\lambda}$ by the transition probability $W_k(\mathbf{r}\,|\,\mathbf{r}')$ for jumps between $\mathbf{r}$ and $\mathbf{r}'$. I make two more assumptions:

(i) That all jumps are small, i.e., that the jump size $|\boldsymbol{\rho}|$, with $\boldsymbol{\rho}\equiv\mathbf{r}-\mathbf{r}'$, is small compared to the distances over which the averages and correlation functions vary appreciably. Note that $|\boldsymbol{\rho}|$ is of the order of the cell diameter.

(ii) that the space is homogeneous and isotropic, so that $W_k(\mathbf{r}\,|\,\mathbf{r}')$ is a function only of the jump size $|\boldsymbol{\rho}|$: $W_k(\mathbf{r}\,|\,\mathbf{r}') = W_k(\rho)$.

Under these conditions (2.23d) can be replaced by the diffusion operator:

$$\sum_{\lambda} W^{(k)}_{\alpha\lambda} \to D_k \Delta \tag{2.24a}$$

where the diffusion constant D_k is related to the matrix $W_k(\mathbf{r}\,|\,\mathbf{r}')$ as

$$D_k = \frac{1}{2d} \int d\boldsymbol{\rho}\, \rho^2 W_k(\rho) \tag{2.24b}$$

Here d is the dimensionality of the system. The approximation (2.24), valid if the jumps are small, is known as the *diffusion approximation.*

Let us collect our results. Start with the macroscopic law, i.e., the rate equation for the averages $\langle m_{k\alpha} \rangle$. Combination of the reaction part (2.11) and the diffusion part (2.20a) yields

$$\begin{aligned} \frac{\partial}{\partial t} \langle u_k(\mathbf{r}, t) \rangle = \frac{1}{2} \sum_{j=0}^{r} A_{kj}(\mathbf{r}, t) \langle u_j(\mathbf{r}, t) \rangle \\ + D_k \Delta \langle u_k(\mathbf{r}, t) \rangle \qquad (k = 0, 1, \ldots, r) \end{aligned} \tag{2.25}$$

The matrix $A_{kj}(\mathbf{r}, t)$ is given by (2.14), with $v^{-1}\langle m_{i\alpha} \rangle \to \langle u_i(\mathbf{r}, t) \rangle$. In (2.25) it is understood that $D_0 = 0$: clusters larger than r do not diffuse. The initial condition for (2.25) is determined by the initial distribution in the cell model, i.e., $\langle u_k(\mathbf{r}, 0) \rangle = m_{k\alpha}(0)/v$. The boundary condition at the surface S of the system is

$$d\mathbf{S} \cdot \frac{\partial}{\partial \mathbf{r}} \langle u_k(\mathbf{r}, t) \rangle = 0 \qquad (\mathbf{r} \in S) \tag{2.26}$$

since jumps across the surface do not occur.

I add several comments. First, Eq. (2.25) with A_{kj} given by (2.14) has the same form as the reaction–diffusion equation (1.8), but now with $D_k = 0$ if $k > r$. Since the parameter r in (2.25) is arbitrary, one can take the limit $r \to \infty$ and find that (1.8) is the correct macroscopic equation both in the pre- and in the post-gel stage. Another remark is that the *gel density* $g(\mathbf{r}, t)$ can now be defined as the limit $r \to \infty$ of the concentrations $\langle u_0(\mathbf{r}, t) \rangle$ in (2.25). As in ref. 17, one concludes that the concept of a "gel" has a meaning *only* in the infinite system, i.e., *after* the Ω-expansion has been applied.

Next consider the fluctuations in $u_k(\mathbf{r}, t)$. In the continuum formulation the covariances $\langle\!\langle m_{k\alpha} m_{l\beta} \rangle\!\rangle$ and the cumulants $[m_{k\alpha} m_{l\beta} \rangle\!\rangle$ are replaced by

$$v^{-2} \langle\!\langle m_{k\alpha} m_{l\beta} \rangle\!\rangle \to \langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \tag{2.27a}$$

$$v^{-2} [m_{k\alpha} m_{l\beta} \rangle\!\rangle \to [u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \tag{2.27b}$$

The relation between these quantities is

$$\begin{aligned} [u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle &= \langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle - \delta_{kl}\delta(\mathbf{r}_1 - \mathbf{r}_2) \langle u_k(\mathbf{r}_1) \rangle \\ &\qquad\qquad (1 \leqslant k, l \leqslant r) \qquad (2.28\text{a}) \\ &= \langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \qquad (k = 0 \text{ or } l = 0) \qquad (2.28\text{b}) \end{aligned}$$

Combination of (2.13) and (2.21) and use of the continuous description (2.23), (2.24), (2.27) yields the following kinetic equation for $[u_k u_l \rangle\!\rangle$:

$$\begin{aligned} &\frac{\partial}{\partial t} [u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \\ &\quad = \sum_{j=0}^{r} \{ A_{kl}(\mathbf{r}_1) [u_j(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle + A_{lj}(\mathbf{r}_2) [u_k(\mathbf{r}_1)\, u_j(\mathbf{r}_2) \rangle\!\rangle \} \\ &\qquad + \delta(\mathbf{r}_1 - \mathbf{r}_2)\, Q_{kl}(\mathbf{r}_1, t) + (D_k \Delta_1 + D_l \Delta_2) [u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \end{aligned} \tag{2.29}$$

Here $Q_{kl}(\mathbf{r}, t)$ is given in (2.15), with $v^{-1} \langle m_{k\alpha} \rangle \to \langle u_k(\mathbf{r}) \rangle$, and $\Delta_i \equiv \partial^2 / \partial \mathbf{r}_i^2$ $(i = 1, 2)$. The initial condition for Eq. (2.29) is

$$\begin{aligned} &[u_k(\mathbf{r}_1, 0)\, u_l(\mathbf{r}_2, 0) \rangle\!\rangle \\ &\quad = -\delta_{kl} \delta(\mathbf{r}_1 - \mathbf{r}_2) \langle u_k(\mathbf{r}_1, 0) \rangle \qquad (1 \leqslant k, l \leqslant r) \qquad (2.30) \\ &\quad = 0 \qquad (k = 0 \text{ or } l = 0) \end{aligned}$$

The boundary condition is again given by (2.26), with $\langle u_k(\mathbf{r}) \rangle$ replaced by $[u_k(\mathbf{r})\, u_l(\mathbf{r}_2) \rangle\!\rangle$. An important restriction on the covariances is imposed by the conservation law for the total mass:

$$\int d\mathbf{r}_1 \left\{ \langle\!\langle u_0(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle + \sum_{k=1}^{r} k \langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \right\} = 0 \tag{2.31a}$$

For the cumulants $[u_k u_l \rangle\!\rangle$ this implies that

$$\begin{aligned} &\int d\mathbf{r}_1 \left\{ [u_0(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle + \sum_{k=1}^{r} k [u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2) \rangle\!\rangle \right\} \\ &\quad = -l \langle u_l(\mathbf{r}_2) \rangle \qquad (1 \leqslant l \leqslant r) \qquad (2.31\text{b}) \\ &\quad = 0 \qquad (l = 0) \end{aligned}$$

Clearly one can take the limit $r \to \infty$ in (2.29), if desired, since the parameter r in (2.29) is arbitrary.

Finally, consider the correlation functions $\kappa_{lk}^{\beta\alpha}(t_2, t_1)$. In the continuum formulation, the correlation functions take the form

$$v^{-2}\kappa_{lk}^{\beta\alpha}(t_2, t_1) \to \kappa_{lk}(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) \tag{2.32a}$$

where

$$\kappa_{lk}(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) \equiv \langle\!\langle u_k(\mathbf{r}_1, t_1)\, u_l(\mathbf{r}_2, t_2)\rangle\!\rangle \tag{2.32b}$$

From (2.19) and (2.22) one finds the following equation for κ_{lk}:

$$\begin{aligned}\frac{\partial}{\partial t}\kappa_{lk}(\mathbf{r}_2, t; \mathbf{r}_1, t_1) = \sum_{j=0}^{r} A_{lj}(\mathbf{r}_2, t)\, \kappa_{jk}(\mathbf{r}_2, t; \mathbf{r}_1, t_1)&\\ + D_l \Delta_2 \kappa_{lk}(\mathbf{r}_2, t; \mathbf{r}_1, t_1)&\end{aligned} \tag{2.33}$$

The initial condition for (2.33) is

$$\kappa_{lk}(\mathbf{r}_2, t_1; \mathbf{r}_1, t_1) = \langle\!\langle u_k(\mathbf{r}_1, t_1)\, u_l(\mathbf{r}_2, t_1)\rangle\!\rangle$$

2.4. Spatially Uniform Initial States

The rest of this section is restricted to the special case[3] where the system is spatially uniform at the initial time $t = 0$, i.e., where $m_{k\lambda}(0) = v m_k(0)/M$ or, in the continuum formulation,

$$u_k(\mathbf{r}, 0) = m_k(0)/M \equiv c_k(0) \qquad (k = 0, 1, \ldots, r) \tag{2.34a}$$

Moreover, I take the thermodynamic limit:

$$M \to \infty, \qquad V \to \infty \tag{2.34b}$$

where the density $M/V = 1$ is kept fixed.

The choice (2.34) is extremely convenient, for various reasons. First, the solution of the macroscopic equation (2.25) with the initial condition (2.34a) is almost trivial. One finds that for all $t \geq 0$

$$\langle u_k(\mathbf{r}, t)\rangle = c_k(t) \qquad (k = 0, 1, \ldots, r) \tag{2.35}$$

where $c_k(t)$ is the solution of Smoluchowski's equation in the form (1.10), with the initial condition $c_k(0)$ in (2.34a). Note that the solution (2.35) satisfies the boundary condition (2.26). Second, if one is interested in spatial fluctuations purely due to the interplay of reactions and diffusion, it

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[3] The more general case, where the initial distribution contains statistical fluctuations about the spatially uniform state, is discussed in Section 5.

is advantageous to eliminate the influence of the initial distribution. This is precisely what is done in (2.34a). Similarly, the choice (2.34b) eliminates the influence of the boundaries.

Apart from the drastic simplification (2.35), the choice (2.34) has the following consequences. The cumulants $[u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2)\rangle\!\rangle$ and the correlation functions $\kappa_{lk}(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1)$ depend on $\mathbf{r}_1$ and $\mathbf{r}_2$ only through the relative coordinates $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$:

$$[u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2)\rangle\!\rangle \equiv E_{kl}(\mathbf{r}, t) \tag{2.36a}$$

$$\kappa_{lk}(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) \equiv \kappa_{lk}(\mathbf{r}; t_2, t_1) \tag{2.36b}$$

More precisely, E_{kl} and κ_{lk} depend on $\mathbf{r}$ only through the relative distance $|\mathbf{r}|$. This follows immediately from the fact that, due to (2.34), both the problem and the initial condition are homogeneous and isotropic.

The equation for the cumulants $E_{kl}(\mathbf{r}, t)$ follows directly from (2.29) as

$$\begin{aligned}\frac{\partial}{\partial t} E_{kl}(\mathbf{r}, t) = {} & \sum_{j=0}^{r} [A_{kj}(t)\, E_{jl}(\mathbf{r}, t) + A_{lj}(t)\, E_{kj}(\mathbf{r}, t)] \\ & + \delta(\mathbf{r})\, Q_{kl}(t) + (D_k + D_l)\, \Delta E_{kl}(\mathbf{r}, t)\end{aligned} \tag{2.37}$$

where I have defined $\Delta \equiv \partial^2/\partial\mathbf{r}^2$. The matrices $A_{kj}(t)$ and $Q_{kl}(t)$ are given by (2.14) and (2.15), with $\langle m_{i\alpha}\rangle/v \to c_i(t)$. The initial value for (2.37) is

$$\begin{aligned} E_{kl}(\mathbf{r}, 0) &= -\delta_{kl}\delta(\mathbf{r})\, c_k(0) \qquad && (1 \leqslant k, l \leqslant r) \\ &= 0 && (k = 0 \text{ or } l = 0) \end{aligned} \tag{2.38}$$

and the boundary condition reduces to $\partial E_{kl}/\partial\mathbf{r} = \mathbf{0}$ at $|\mathbf{r}| = \infty$. An important property is

$$\begin{aligned} \int d\mathbf{r} \left[E_{0l}(\mathbf{r}, t) + \sum_{k=1}^{r} k E_{kl}(\mathbf{r}, t) \right] &= -l c_l(t) \qquad && (1 \leqslant l \leqslant r) \\ &= 0 && (l = 0) \end{aligned} \tag{2.39}$$

This is the mass conservation law (2.31) for systems with a spatially uniform initial state.

The correlation functions $\kappa_{lk}(\mathbf{r}; t, t_1)$ satisfy the following linear equation due to (2.33):

$$\frac{\partial}{\partial t} \kappa_{lk}(\mathbf{r}; t, t_1) = \sum_{j=0}^{r} A_{lj}(t)\, \kappa_{jk}(\mathbf{r}; t, t_1) + D_l\, \Delta\kappa_{lk}(\mathbf{r}; t, t_1) \tag{2.40}$$

to be solved with the initial condition that for $t \downarrow t_1$, $\kappa_{lk}(\mathbf{r}; t, t_1)$ reduces to the covariances.

In order to solve Eq. (2.37) for $E_{kl}(\mathbf{r}, t)$, it is convenient to introduce the Fourier transform

$$F_{kl}(\mathbf{q}, t) \equiv \int d\mathbf{r}\, [\exp(i\mathbf{q}\cdot\mathbf{r})]\, E_{kl}(\mathbf{r}, t) \tag{2.41}$$

which satisfies, for each fixed value of $\mathbf{q}$, a set of coupled ordinary differential equations:

$$\begin{aligned}\frac{\partial}{\partial t} F_{kl}(\mathbf{q}, t) = \sum_{j=0}^{r} [A_{kj}(t)\, F_{jl}(\mathbf{q}, t) + A_{lj}(t)\, F_{kj}(\mathbf{q}, t)] + Q_{kl}(t)\\ - (D_k + D_l)\, q^2 F_{kl}(\mathbf{q}, t)\end{aligned} \tag{2.42a}$$

Note that $F_{kl}(\mathbf{q}, t)$ depends on $\mathbf{q}$ only through its modulus $|\mathbf{q}|$. The initial condition for (2.42a) follows from (2.38) as

$$\begin{aligned} F_{kl}(\mathbf{q}, 0) &= -\delta_{kl} c_k(0) \qquad (1 \leqslant k, l \leqslant r)\\ &= 0 \qquad (k = 0 \text{ or } l = 0)\end{aligned} \tag{2.42b}$$

The mass conservation law (2.39), in terms of $F_{kl}(\mathbf{q}, t)$, reads

$$\begin{aligned} F_{0l}(\mathbf{0}, t) + \sum_{k=1}^{r} kF_{kl}(\mathbf{0}, t) &= -lc_l(t) \qquad (1 \leqslant l \leqslant r)\\ &= 0 \qquad (l = 0)\end{aligned} \tag{2.43}$$

Similarly, to solve Eq. (2.40), it is convenient to introduce the Fourier transform $\hat{\kappa}_{lk}$ of κ_{lk}, which satisfies the following set of equations:

$$\frac{\partial}{\partial t} \hat{\kappa}_{lk}(\mathbf{q}; t, t_1) = \sum_{j=0}^{r} A_{lj}(t)\, \hat{\kappa}_{jk}(\mathbf{q}; t, t_1) - D_l q^2 \hat{\kappa}_{lk}(\mathbf{q}; t, t_1) \tag{2.44}$$

Equations (2.42)–(2.44) are the starting point for the calculations in Sections 3 and 4.

Before concluding, I remark that Eqs. (2.42) for F_{kl} and (2.44) for $\hat{\kappa}_{lk}$ have an important special case, $\mathbf{q} = \mathbf{0}$. Comparison of Eq. (2.42) for $\mathbf{q} = \mathbf{0}$ with Eq. (2.23a) of ref. 17 shows that $F_{kl}(\mathbf{0}, t)$ is identical to the (factorial) cumulants of the nonspatial problem. More precisely, one finds for $1 \leqslant k$, $l \leqslant r$ that

$$F_{kl}(\mathbf{0}, t) = \int d\mathbf{r}\, E_{kl}(\mathbf{r}, t) = e_{kl}(t) \qquad (1 \leqslant k, l \leqslant r) \tag{2.45a}$$

where e_{kl} is the factorial cumulant $v^{-1}[m_k m_l]$ of ref. 17. For $l=0$ and $k \neq 0$ one has

$$F_{0k}(\mathbf{0}, t) = F_{k0}(\mathbf{0}, t) = \langle\langle \xi_k \gamma_r \rangle\rangle$$

$$= -\left(kc_k + \sum_{l=1}^{r} le_{lk}\right) \qquad (1 \leqslant k \leqslant r) \qquad (2.45\text{b})$$

Finally, if both $k=0$ and $l=0$,

$$F_{00}(\mathbf{0}, t) = \langle\langle (\gamma_r)^2 \rangle\rangle$$

$$= \sum_{k,l=1}^{r} kle_{kl} + \sum_{l=1}^{r} l^2 c_l \qquad (2.45\text{c})$$

Here $\xi_k = v^{-1/2}\, \Delta m_k$ is the fluctuation in the number of k-mers, and $\gamma_r = v^{-1/2}\, \Delta m_0$ is the fluctuation in the mass of clusters larger than r. Similarly, one finds that $\hat{\kappa}_{lk}(\mathbf{0}; t_2, t_1)$ is identical to the correlation functions of the nonspatial problem. In the notation of ref. 17, one has for $1 \leqslant k$, $l \leqslant r$

$$\hat{\kappa}_{lk}(\mathbf{0}; t_2, t_1) = \kappa_{lk}(t_2, t_1) \qquad (1 \leqslant k, l \leqslant r) \qquad (2.46)$$

whereas for $k=0$ or $l=0$, $\hat{\kappa}_{lk}(\mathbf{0}; t_2, t_1)$ is in an obvious way related to the correlation functions for the mass contained in clusters larger than r. The identifications (2.45) and (2.46) hold for a general (but spatially uniform) initial distribution $c_k(0)$ and for all possible choices of the parameter r and the diffusion constants D_k. This shows that the nonspatial cumulants and correlation functions, considered in ref. 17, also have great significance for the reaction–diffusion problem considered in this paper.

3. AN EXACTLY SOLUBLE MODEL FOR THE PRE-GEL STAGE

This section is restricted to the pre-gel stage ($t < t_c$), where there is no gel, so that (for $r \to \infty$) all correlation functions E_{kl} and κ_{lk} with $k=0$ or $l=0$ vanish. A model is presented for which the kinetic equations derived in Section 2.4 can be solved exactly. The diffusion constants characterizing this model are given by

$$D_k = D \qquad (k = 1, 2, \ldots) \qquad (3.1\text{a})$$

i.e., the diffusion constant is chosen to be *independent of the cluster size.* The presentation is restricted to *monodisperse initial conditions*, corresponding to

$$u_k(\mathbf{r}, 0) = \delta_{k1} \qquad (3.1\text{b})$$

The equal-time correlation functions (covariances) are calculated in Section 3.1, the two-time correlation functions in Section 3.2. The covariances may also be calculated exactly (in terms of their generating function) for general initial conditions $u_k(\mathbf{r}, 0) = c_k(0)$. These results for general initial conditions are presented in the Appendix.

3.1. The Equal-Time Correlation Functions

To calculate the covariances $\langle\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2)\rangle\rangle$, let us consider first the cumulants[4] $E_{kl}(\mathbf{r}, t)$ in (2.37) or, rather, their Fourier transform $F_{kl}(\mathbf{q}, t)$. The Fourier transform F_{kl} may be calculated from Eq. (2.42) with $r = \infty$ and $D_k = D$. In the pre-gel stage, Eq. (2.42) reduces to

$$\frac{\partial}{\partial t} F_{kl}(\mathbf{q}, t) = \sum_{j=1}^{\infty} [A_{kj} F_{jl} + A_{lj} F_{kj}] + Q_{kl} - 2Dq^2 F_{kl} \tag{3.2a}$$

where in this case $k, l = 1, 2, \ldots$. The matrices A_{kj} and Q_{kl} are given by

$$A_{kj}(t) = -\sum_{i=1}^{\infty} K_{ij}(\delta_{ik} + \delta_{jk} - \delta_{i+j,k})\, c_i(t) \tag{3.2b}$$

$$Q_{kl}(t) = -klc_k(t)\, c_l(t) \tag{3.2c}$$

Equations (3.2b) and (3.2c) follow directly from (2.14a) and (2.15a), with $\langle m_{i\alpha}\rangle / v \to c_i(t)$ and $r = \infty$.

In the Appendix, Eq. (3.2) is solved for general initial conditions with the use of generating function techniques. For monodisperse initial conditions, this result for the generating function may be inverted to yield the following, surprisingly simple, expression for $F_{kl}(\mathbf{q}, t)$:

$$F_{kl}(\mathbf{q}, t) = e_{kl}(t)\, \chi(\mathbf{q}, t) \tag{3.3a}$$

where

$$\chi(\mathbf{q}, t) \equiv (1 - t)\, e^{-2Dq^2 t} \left[1 + \int_0^t d\tau\, (1 - \tau)^{-2}\, e^{2Dq^2 \tau} \right] \tag{3.3b}$$

and $e_{kl}(t)$ is the factorial cumulant of the nonspatial problem, discussed in ref. 17:

$$e_{kl}(t) = -(1 - t)\, klc_k(t)\, c_l(t) \tag{3.3c}$$

Here $c_k(t)$ is the concentration of k-mers, given in (1.13).

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[4] Note that in the pre-gel stage E_{kl} (with $k, l = 1, 2, \ldots$) is simply a *factorial* cumulant.

We can verify, by inserting (3.3) into (3.2), that (3.3) is indeed the solution of (3.2). Substitution of (3.3a) into the left-hand side of (3.2a) gives

$$\text{LHS}(3.2\text{a}) = \dot{e}_{kl}\chi(\mathbf{q}, t) + e_{kl}\frac{\partial}{\partial t}\chi(\mathbf{q}, t) \tag{3.4a}$$

Similarly, the right-hand side of (3.2a) yields

$$\begin{aligned}\text{RHS}(3.2\text{a}) &= \chi\left\{\sum_j (A_{kj}e_{jl} + A_{lj}e_{kj}) - 2Dq^2 e_{kl}\right\} - klc_k c_l \\ &= \chi\{\dot{e}_{kl} + klc_k c_l - 2Dq^2 e_{kl}\} - klc_k c_l\end{aligned} \tag{3.4b}$$

The second step of (3.4b) uses the fact that $e_{kl}(t)$ satisfies Eq. (3.2a) for $\mathbf{q} = \mathbf{0}$ [see the discussion around (2.45a)]. Comparison of Eqs. (3.4a) and (3.4b), in combination with Eq. (3.3c) for $e_{kl}(t)$, shows that $F_{kl}(\mathbf{q}, t)$ in (3.3a) is indeed the solution of Eq. (3.2), provided that $\chi(\mathbf{q}, t)$ satisfies the following ordinary differential equation:

$$\frac{\partial\chi}{\partial t} + [(1-t)^{-1} + 2Dq^2]\chi = (1-t)^{-1} \tag{3.5}$$

The initial condition for (3.5) is $\chi(\mathbf{q}, 0) = 1$, as may be seen from a comparison of (2.42b) and (3.3a) for $t = 0$ and $k = l = 1$. The solution of (3.5), satisfying $\chi(\mathbf{q}, 0) = 1$, is given by (3.3b). Note that $F_{kl}(\mathbf{q}, t)$ in (3.3) satisfies the condition (2.45a) for all $t < t_c = 1$.

Equation (3.3) for the Fourier transform $F_{kl}(\mathbf{q}, t)$ may readily be inverted to yield the factorial cumulants $E_{kl}(\mathbf{r}, t)$. To do this, it is convenient to introduce the d-dimensional Gaussian distribution with zero mean and variance σ^2:

$$g(\mathbf{r}; \sigma^2) \equiv (2\pi\sigma^2)^{-d/2} \exp(-\mathbf{r}^2/2\sigma^2) \tag{3.6a}$$

which has

$$\int d\mathbf{r}\, g(\mathbf{r}; \sigma^2) \exp(i\mathbf{q}\cdot\mathbf{r}) = \exp(-\tfrac{1}{2}\sigma^2 q^2) \tag{3.6b}$$

as its Fourier transform. From (3.3b) and (3.6) one can infer that $E_{kl}(\mathbf{r}, t)$ takes the form

$$E_{kl}(\mathbf{r}, t) = e_{kl}(t)\, G(\mathbf{r}, t) \tag{3.7a}$$

with $G(\mathbf{r}, t)$ given by

$$G(\mathbf{r}, t) = (1-t)\left[g(\mathbf{r}; 4Dt) + \int_0^t d\tau\,(1-\tau)^{-2}\,g(\mathbf{r}; 4D(t-\tau))\right] \tag{3.7b}$$

As an immediate consequence, one finds the following expression for the covariances, due to (2.28a):

$$\langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2)\rangle\!\rangle = e_{kl}(t)\, G(\mathbf{r}, t) + \delta_{kl}\delta(\mathbf{r})\, c_k(t) \tag{3.8}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and $c_k(t)$ is given in (1.13). The second term on the right in (3.8) is a Poisson term, and would be the only term if all numbers $u_k(\mathbf{r})$ would be taken from independent Poisson distributions. The first term on the right is always *negative* if $t < 1$ (sub-Poisson distribution). This can be viewed as an effect of the mass conservation law: a positive fluctuation in the number of k-mers at $\mathbf{r}_1$ implies that, most likely, there will be fewer l-mers at $\mathbf{r}_2$.

A quantity of considerable interest that can be calculated directly from (3.8) is the density–density correlation function, i.e.,

$$\rho(\mathbf{r}, t) \equiv \sum_{k,l} kl \langle\!\langle u_k(\mathbf{r}_1)\, u_l(\mathbf{r}_2)\rangle\!\rangle \tag{3.9}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. An expression for $\rho(\mathbf{r}, t)$ is obtained by multiplying (3.8) with kl and summing over all k and l. The result is

$$\rho(\mathbf{r}, t) = (1-t)^{-1}\,[\delta(\mathbf{r}) - G(\mathbf{r}, t)] \tag{3.10}$$

The derivation of (3.10) used (3.3c) and the explicit form of the second moment of $c_k(t)$, i.e.,

$$M_2(t) \equiv \sum_{k=1}^{\infty} k^2 c_k(t) = (1-t)^{-1} \qquad (t < 1) \tag{3.11}$$

An expression for the Fourier transform $\hat{\rho}(\mathbf{q}, t)$ of $\rho(\mathbf{r}, t)$ follows immediately from (3.10) as

$$\hat{\rho}(\mathbf{q}, t) = (1-t)^{-1}\,[1 - \chi(\mathbf{q}, t)] \tag{3.12}$$

since $\chi(\mathbf{q}, t)$ and $G(\mathbf{r}, t)$ are related by Fourier transformation.

What happens when the system approaches the gel point $t_c = 1$? To see this, consider Eq. (3.3b) for $\chi(\mathbf{q}, t)$. In the limit $t \uparrow 1$ one finds that

$$\chi(\mathbf{q}, t) \to 1 \qquad (t \uparrow 1) \tag{3.13a}$$

irrespective of the value of $\mathbf{q}$. In terms of $G(\mathbf{r}, t)$ this implies that

$$G(\mathbf{r}, t) \to \delta(\mathbf{r}) \qquad (t \uparrow 1) \tag{3.13b}$$

Thus, we arrive at our first conclusion: as $t \uparrow t_c$, the covariances $\langle\!\langle u_k u_l \rangle\!\rangle$ in (3.8) assume the form of a delta peak, implying that the width of the spatial profile of the fluctuations *vanishes* near the phase transition.

The leading behavior (3.13) yields insufficient information to study the behavior of the density fluctuations as $t \uparrow t_c$. This may be seen directly from (3.10) or (3.12). The next order in (3.13a) is

$$\chi(\mathbf{q}, t) = 1 + 2Dq^2(1-t)\ln(1-t) + O(1-t) \qquad (t \uparrow 1) \tag{3.14}$$

so that

$$\hat{\rho}(\mathbf{q}, t) \sim -2Dq^2 \ln(1-t) \to \infty \qquad (t \uparrow 1) \tag{3.15}$$

Hence the second conclusion is that the density fluctuations diverge at all length scales as $t \uparrow t_c$ or, alternatively, that the spatial fluctuations in the density are extremely large. An immediate consequence is that the continuum approximation, which is based on the assumption that the correlation functions are smooth, breaks down shortly before t_c: the present methods *cannot* be used to study the model $D_k = D$ in the post-gel stage. Physically this is obvious: in the model (3.1) large clusters are much too mobile. Due to this large mobility, large clusters can be brought together to react, whereas they would stay apart without diffusion. In this manner large clusters contribute significantly to the fluctuations in the density, particularly in the vicinity of the gel point.

3.2. The Two-Time Correlation Functions

Next consider the behavior in the pre-gel stage of the correlation functions $\hat{\kappa}_{lk}(\mathbf{q}; t, t_1)$, which satisfy Eq. (2.44) with $k, l = 1, 2,\ldots$ and $r = \infty$, i.e.,

$$\frac{\partial}{\partial t}\hat{\kappa}_{lk}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} A_{lj}(t)\,\hat{\kappa}_{jk}(\mathbf{q}; t, t_1) - Dq^2\hat{\kappa}_{lk}(\mathbf{q}; t, t_1) \tag{3.16a}$$

The matrix A_{lj} is given in (3.2b). The initial condition for (3.16a) follows from the fact that, for $t \downarrow t_1$, $\hat{\kappa}_{lk}(\mathbf{r}; t, t_1)$ reduces to the covariances

$$\hat{\kappa}_{lk}(\mathbf{q}; t_1, t_1) = F_{lk}(\mathbf{q}, t_1) + \delta_{lk} c_k(t_1) \tag{3.16b}$$

Equation (3.16) may be solved in two steps. In the first step, eliminate the explicit $\mathbf{q}$ dependence in (3.16a) by transforming from $\hat{\kappa}_{lk}$ to a new function a_{lk}, defined as

$$a_{lk}(\mathbf{q}; t, t_1) \equiv \hat{\kappa}_{lk}(\mathbf{q}; t, t_1)\, e^{Dq^2(t-t_1)} \tag{3.17}$$

Substitution of (3.17) into (3.16a) and use of the explicit form (3.2b) of the matrix $A_{kj}(t)$ shows that a_{lk} satisfies the following set of ordinary differential equations:

$$\begin{aligned}\frac{\partial}{\partial t} a_{lk}(\mathbf{q}; t, t_1) &= \sum_{j=1}^{\infty} A_{lj}(t)\, a_{jk}(\mathbf{q}; t, t_1)\\ &= -lc_l \sum_j j a_{jk} - l a_{lk} + \sum_{i+j=l} ij c_i a_{jk}\end{aligned} \tag{3.18a}$$

The initial condition for Eq. (3.18a) is the same as for $\hat{\kappa}_{lk}(\mathbf{q}; t_1, t_1)$, i.e.,

$$a_{lk}(\mathbf{q}; t_1, t_1) = F_{kl}(\mathbf{q}, t_1) + \delta_{kl} c_k(t_1) \tag{3.18b}$$

Note that a_{lk} depends upon $\mathbf{q}$ only through the initial condition.

The second step in the calculation of $\hat{\kappa}_{lk}$ is to eliminate the first term on the right in (3.18a). To do this, observe that the sum $\sum_j j a_{jk}$ is constant for all $t < t_c$:

$$\sum_j j a_{jk}(\mathbf{q}; t, t_1) = \text{const} \equiv \alpha_k(\mathbf{q}, t_1) \qquad (t_1 \leqslant t < t_c = 1) \tag{3.19a}$$

This may readily be demonstrated from Eq. (3.18a) by multiplying this equation with l and summing over all l. The value of $\alpha_k(\mathbf{q}, t_1)$ follows from (3.18b), (3.3), and (3.11) as

$$\alpha_k(\mathbf{q}, t_1) = kc_k(t_1)[1 - \chi(\mathbf{q}, t_1)] \tag{3.19b}$$

Furthermore, let us transform from a_{lk} to new functions b_{lk} defined as

$$b_{lk}(\mathbf{q}; t, t_1) \equiv a_{lk}(\mathbf{q}; t, t_1) + lc_l(t)\, \alpha_k(\mathbf{q}, t_1)(t - t_1) \tag{3.20}$$

and satisfying an equation of the form (3.18a), but now without the first term on the right-hand side:

$$\frac{\partial}{\partial t} b_{lk}(\mathbf{q}; t, t_1) = \sum_{i+j=l} ij c_i(t)\, b_{jk}(\mathbf{q}; t, t_1) - l b_{lk}(\mathbf{q}; t, t_1) \tag{3.21}$$

The initial condition for b_{lk} is the same as that for a_{lk}, given in (3.18b).

The problem (3.21) has been solved in ref. 17. The result is that $b_{lk}(\mathbf{q}; t, t_1)$ is linearly related to its initial value at $t = t_1$ as follows:

$$b_{lk}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} Y_{lj}(t, t_1)\, b_{jk}(\mathbf{q}; t_1, t_1) \tag{3.22a}$$

where the evolution matrix $Y_{lj}(t, t_1)$ is given by

$$Y_{lj}(t, t_1) = j(t - t_1)\frac{(lt - jt_1)^{l-j-1}}{(l-j)!}\, e^{jt_1 - lt} \tag{3.22b}$$

The matrix Y_{lj} has the property

$$\sum_{j=1}^{\infty} Y_{lj}(t, t_1)\, jc_j(t_1) = lc_l(t) \tag{3.23}$$

From Eqs. (3.17), (3.20), (3.22a), and (3.23) it then follows that $\hat{\kappa}_{lk}(\mathbf{q}; t_2, t_1)$ is related in a simple way to the correlation functions $\kappa_{lk}(t_2, t_1)$ of the nonspatial problem [see (2.46)]

$$\begin{aligned}\hat{\kappa}_{lk}(\mathbf{q}; t_2, t_1) = e^{-Dq^2(t_2 - t_1)}\{&\kappa_{lk}(t_2, t_1)\\ &+ (1 - t_2)\, klc_k(t_1)\, c_l(t_2)[1 - \chi(\mathbf{q}, t_1)]\}\end{aligned} \tag{3.24a}$$

The explicit form of $\kappa_{lk}(t_2, t_1)$ has been calculated in ref. 17. The result is

$$\kappa_{lk}(t_2, t_1) = Y_{lk}(t_2, t_1)\, c_k(t_1) - (1 - t_1)\, klc_k(t_1)\, c_l(t_2) \tag{3.24b}$$

Note that $\hat{\kappa}_{lk}$ in (3.24a) reduces to $\kappa_{lk}(t_2, t_1)$ for $\mathbf{q} = \mathbf{0}$. Further note that the second term on the right in (3.24a) vanishes if t_2 is chosen at the gel point ($t_2 = 1$).

Equation (3.24) may be inverted with the use of (3.6) to yield an expression for the correlation functions $\kappa_{lk}(\mathbf{r}; t_2, t_1)$. The result is

$$\begin{aligned}\kappa_{lk}(\mathbf{r}; t_2, t_1) = {}&\kappa_{lk}(t_2, t_1)\, g(\mathbf{r}; 2D(t_2 - t_1))\\ &+ (1 - t_2)\, klc_k(t_1)\, c_l(t_2)[g(\mathbf{r}; 2D(t_2 - t_1)) - G(\mathbf{r}; t_2, t_1)]\end{aligned} \tag{3.25a}$$

where

$$\begin{aligned}G(\mathbf{r}; t_2, t_1) = (1 - t_1)\Big[&g(\mathbf{r}; 2D(t_1 + t_2))\\ &+ \int_0^{t_1} d\tau\, (1 - \tau)^{-2}\, g(\mathbf{r}; 2D(t_2 + t_1 - 2\tau))\Big]\end{aligned} \tag{3.25b}$$

Thus $\kappa_{lk}(\mathbf{r}; t_2, t_1)$ is a superposition of Gaussians. The first two terms in (3.25a) correspond to correlations formed between t_1 and t_2. The last term, proportional to $G(\mathbf{r}; t_2, t_1)$, represents correlations spreading since $t = 0$ [first term on the rhs of (3.25b)] or since some time t' with $0 < t' < t_1$ [second term on the rhs of (3.25b)].

An interesting interpretation of Eq. (3.25a) may be obtained as follows. Consider the fluctuations in the mass density, which [for D_k as in (3.1)] are purely due to diffusion. The correlation function $\rho(\mathbf{r}; t_2, t_1)$ for the mass density is defined as

$$\rho(\mathbf{r}; t_2, t_1) \equiv \sum_{k,l} kl \langle\langle u_k(\mathbf{r}_1, t_1)\, u_l(\mathbf{r}_2, t_2) \rangle\rangle \tag{3.26}$$

(with $\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$), and may be calculated from (3.25a) by multiplying with kl and summing over all k and l. The result is

$$\rho(\mathbf{r}; t_2, t_1) = (1 - t_1)^{-1} [g(\mathbf{r}; 2D(t_2 - t_1)) - G(\mathbf{r}; t_2, t_1)] \tag{3.27}$$

In the derivation of (3.27), Eq. (3.11) was used for $M_2(t)$. Note that the first term in (3.25a) does not contribute to $\rho(\mathbf{r}; t_2, t_1)$, due to (3.24b) and (3.22b). Thus, one arrives at the following interpretation of Eq. (3.25a). The *first term* on the right, proportional to the nonspatial correlation functions $\kappa_{lk}(t_2, t_1)$, represents the fluctuations within each cell, purely due to *reactions*. The *second term*, proportional to $\rho(\mathbf{r}; t_2, t_1)$, represents the fluctuations in the mass density and hence is purely due to *diffusion*. A similar interpretation holds of course for (3.8), which can be obtained from (3.25) by setting $t_2 = t_1$.

4. FLUCTUATIONS IN THE POST-GEL STAGE

In the previous section it was shown that the model (3.1), i.e., $D_k = D$ (all k), leads to a divergence of the density fluctuations as $t \uparrow t_c$. For this model the method of this paper breaks down at the gel point. In this section I show that the divergence of the density fluctuations at the gel point is an artefact of the model (3.1), where large and small clusters are equally mobile.

Therefore, to study the post-gel stage, we want a model where small clusters are mobile and large clusters are not. The simplest model of this form is

$$D_k = D \quad (k = 1,..., s); \qquad D_k = 0 \quad (k > s) \tag{4.1}$$

The cluster size s in (4.1) represents the boundary between small and large clusters. As it turns out, the model (4.1) is still too complicated to be solved in all detail. I have only been able to calculate the *covariances*. The solution is valid only if the initial state is *monodisperse* [see (3.1b)]. Even then, some of the results are not very explicit. Nevertheless, one can extract sufficient information to study the post-gel stage.

Let us start from Eq. (2.42) for the Fourier transform $F_{kl}(\mathbf{q}, t)$ of the cumulants $E_{kl}(\mathbf{r}, t)$. In the derivation of (2.42) it has been assumed that $D_k = 0$ for all $k > r$. Hence, any equation of the form (2.42) can be used to study the model (4.1), provided that $r \geqslant s$. Below I choose $r = s$.

The solution of (2.42) for $\mathbf{q} = \mathbf{0}$ was found in Section 2, Eq. (2.45). A convenient short-hand notation is $F_{kl}(\mathbf{0}, t) = e_{kl}(t)$, where

$$e_{kl}(t) = -(1-t)\, klc_k(t)\, c_l(t) \qquad (1 \leqslant k, l \leqslant s) \tag{4.2a}$$

$$e_{k0}(t) = e_{0k}(t) = -kc_k(t)[1 + (t-1)\, M_2^{(s)}(t)] \qquad (1 \leqslant k \leqslant s) \tag{4.2b}$$

$$e_{00}(t) = M_2^{(s)}(t)[1 + (t-1)\, M_2^{(s)}(t)] \tag{4.2c}$$

In (4.2) I introduced the partial moments $M_\alpha^{(s)}(t) \equiv \sum_{k=1}^{s} k^\alpha c_k(t)$. Note that $M_2^{(s)}(t)$ has a *finite* peak near the gel point t_c. This peak is higher for larger values of s.

A subtle point that becomes relevant in this section is the *initial condition* for Eq. (2.42). In the present case, the condition formulated in (2.42b) is too weak. This may be seen as follows. At the initial time $t = 0$ the fluctuations are delta correlated, i.e., the spatial profile of $E_{kl}(\mathbf{r}, t)$ reduces to a delta function as $t \downarrow 0$. This information is lost in (2.38) if it so happens that the prefactor of $\delta(\mathbf{r})$ vanishes for $t = 0$; hence, it is always lost for $k = 0$ or $l = 0$. This defect may be cured by imposing the stronger initial condition

$$E_{kl}(\mathbf{r}, t) \Big/ \int d\mathbf{r}\, E_{kl}(\mathbf{r}, t) \to \delta(\mathbf{r}) \qquad (t \downarrow 0) \tag{4.3a}$$

or, equivalently,

$$F_{kl}(\mathbf{q}, t)/e_{kl}(t) \to 1 \qquad (t \downarrow 0) \tag{4.3b}$$

where $e_{kl}(t)$ is given in (4.2).

The solution of Eq. (2.42a) for $F_{kl}(\mathbf{q}, t)$, with the initial condition (4.3b), $r = s$, and D_k as in (4.1), has a very simple form for all $t \geqslant 0$, namely

$$F_{kl}(\mathbf{q}, t) = -klc_k(t)\, c_l(t)\, \chi_1(\mathbf{q}, t) \qquad (1 \leqslant k, l \leqslant s) \tag{4.4a}$$

$$F_{k0}(\mathbf{q}, t) = e_{k0}(t)\, \chi_2(\mathbf{q}, t) \qquad (1 \leqslant k \leqslant s) \tag{4.4b}$$

$$F_{00}(\mathbf{q}, t) = e_{00}(t)\, \chi_3(\mathbf{q}, t) \tag{4.4c}$$

Thus, the k, l and the $\mathbf{q}$ dependences in F_{kl} separate, as was found for the pre-gel solution (3.3a) in Section 3. Note that the k, l dependence of F_{kl} is the same as that of the nonspatial cumulants e_{kl} in (4.2). The form of $\chi_i(\mathbf{q}, t)$ $(i = 1, 2, 3)$ for $\mathbf{q} = \mathbf{0}$ follows immediately from (4.2) as (all $t \geqslant 0$)

$$\begin{aligned} \chi_1(\mathbf{0}, t) &= 1 - t \\ \chi_2(\mathbf{0}, t) &= \chi_3(\mathbf{0}, t) = 1 \end{aligned} \tag{4.5}$$

Furthermore, the initial condition for $\chi_i(\mathbf{q}, t)$ is

$$\chi_i(\mathbf{q}, 0) = 1 \qquad (i = 1, 2, 3) \tag{4.6}$$

This follows directly from Eq. (4.3).

To verify that (4.4) represents a solution of the kinetic equation (2.42a), substitute (4.4) into (2.42a) and find that (4.4) is indeed the solution, provided that the functions $\chi_i(\mathbf{q}, t)$ satisfy the following coupled differential equations:

$$\dot{\chi}_1(\mathbf{q}, t) = 1 - 2[1 + (t-1)\, M_2^{(s)}(t)]\, \chi_2 - 2[M_2^{(s)}(t) + Dq^2]\, \chi_1 \tag{4.7a}$$

$$\begin{aligned} \dot{\chi}_2(\mathbf{q}, t) = {} & M_2^{(s)}(t)\, Q_{00}(t)[\chi_1 + (t-1)\, \chi_2]/e_{00}(t) \\ & + (\chi_3 - \chi_2)\, M_2^{(s)}(t) - Dq^2 \chi_2 \end{aligned} \tag{4.7b}$$

$$\dot{\chi}_3(\mathbf{q}, t) = -2Q_{00}(t)(\chi_2 - \chi_3)/M_2^{(s)}(t) + (1 - \chi_3)\, Q_{00}(t)/e_{00}(t) \tag{4.7c}$$

The matrix elements Q_{kl} have been defined in (2.15c). Recall that

$$Q_{00}(t) = \frac{1}{2} \sum_{i,j=1}^{s} K_{ij}(i+j)^2\, \eta_{i+j-s} c_i(t)\, c_j(t) + c_0(t)\, M_3^{(s)}(t) \tag{4.8}$$

where $c_0(t)$ represents the mass of clusters larger than s. The derivation of (4.7) used the fact that the cumulants $\dot{e}_{kl}(t)$ in (4.2) satisfy Eq. (2.42a) with $\mathbf{q} = \mathbf{0}$. Furthermore, the explicit form of the matrix A_{kl} was used in (2.14) to show that $\sum_{k=1}^{s} kA_{0k}c_k = Q_{00}$. Note that Eq. (4.7) has the structure of a linear, inhomogeneous, first-order differential equation for the vector $\boldsymbol{\chi}(\mathbf{q}, t)$:

$$\frac{\partial}{\partial t} \boldsymbol{\chi}(\mathbf{q}, t) = B(t)\, \boldsymbol{\chi}(\mathbf{q}, t) + \boldsymbol{\psi}(t) \tag{4.9}$$

where $B(t)$ is a 3×3 matrix. The solution can formally be written as a time-ordered exponential (see ref. 5, Section XIV.7), but such expressions are not very transparent, and can be omitted here. Nevertheless, this result has two important consequences. First, the solution of (4.9) with the initial condition (4.6) is unique. Second, the solution is finite for all finite values of t.

Before analyzing the detailed behavior of $\boldsymbol{\chi}(\mathbf{q}, t)$ in (4.7), let us consider the density fluctuations in the model (4.1). From the definition

$$\rho(\mathbf{r}, t) = \left\langle\!\!\left\langle \left[\sum_{k=1}^{s} k u_k(\mathbf{r}_1) + u_0(\mathbf{r}_1) \right] \left[\sum_{l=1}^{s} l u_l(\mathbf{r}_2) + u_0(\mathbf{r}_2) \right] \right\rangle\!\!\right\rangle \tag{4.10}$$

it follows that the Fourier transform $\hat{\rho}(\mathbf{q}, t)$ of $\rho(\mathbf{r}, t)$ is given by

$$\begin{aligned}\hat{\rho}(\mathbf{q}, t) &= \sum_{k,l=1}^{s} kl(F_{kl} + \delta_{kl}c_k) + 2\sum_{k=1}^{s} kF_{k0} + F_{00} \\ &= M_2^{(s)}(t) - \chi_1(\mathbf{q}, t)[M_2^{(s)}(t)]^2 + [\chi_3(\mathbf{q}, t) - 2\chi_2(\mathbf{q}, t)]\, e_{00}(t) \qquad (4.11)\end{aligned}$$

This result is finite for all $t \geq 0$ due to the finiteness of $\chi(\mathbf{q}, t)$. This leads to my first conclusion: the divergence of $\hat{\rho}(\mathbf{q}, t)$ at t_c in Section 3 is an artefact of the model (3.1).

In the following I analyze the behavior of the functions $\chi_i(\mathbf{q}, t)$ for various combinations of $\mathbf{q}$ and t. Four different limits will be studied: the limits of large and small wave vectors ($q \to \infty$ and $q \to 0$), the limit $t \to \infty$, and, finally, the limit $s \to \infty$. These limits are treated separately; the results are presented in Sections 4.1–4.4. From these results I calculate the upper critical dimension (Section 4.5). Section 4.6 formulates the conclusions.

4.1. The Limit $q \to \infty$

The behavior of $\chi_i(\mathbf{q}, t)$ for $q \to \infty$ corresponds to correlations at *short* distances. Recall from (4.3) that, initially, the fluctuations are delta correlated, leading to the finite value $\chi_i(\infty, 0) = 1$ in (4.6). For all $t > 0$ the delta functions in $\chi_1(\mathbf{q}, t)$ and $\chi_2(\mathbf{q}, t)$ have broadened due to the diffusion terms in (4.7a), (4.7b). Hence, one expects that, for all $t > 0$, $\chi_1(\infty, t) = \chi_2(\infty, t) = 0$. No diffusion occurs for clusters of size $k > s$ (corresponding to χ_3). Hence, one expects $\chi_3(\infty, t) > 0$ for all $t > 0$.

To show that these ideas lead to a consistent large-q solution, consider Eq. (4.7c) for $\chi_3(\mathbf{q}, t)$. Elementary integration, with $\chi_2(\infty, t) = 0$, yields

$$\chi_3(\infty, t) = 1 + \int_0^t dt'\, I_s(t, t') \qquad (4.12a)$$

where

$$I_s(t, t') = 2\frac{Q_{00}(t')}{M_2^{(s)}(t')} \exp\left\{-\int_{t'}^{t} dt'' \left(\frac{Q_{00}(t'')}{e_{00}(t'')} - 2\frac{Q_{00}(t'')}{M_2^{(s)}(t'')}\right)\right\} \qquad (4.12b)$$

Since $Q_{00}(t) > 0$ for all $t > 0$, it can be inferred from (4.12) that $\chi_3(\infty, t) > 1$ for all $t > 0$, i.e., that local correlations between large clusters are more pronounced for $t > 0$ than they are at $t = 0$. Note that these correlations are finite: $\chi_3(\infty, t) < \infty$ (all $t < \infty$). Let us calculate the large-q behavior of χ_1 and χ_2. Formal integration of Eqs. (4.7b) and (4.7a) shows that for $q \to \infty$

$$\chi_2(\mathbf{q}, t) \sim \chi_3(\infty, t)\, M_2^{(s)}(t)/Dq^2 \qquad (q \to \infty) \qquad (4.13a)$$

$$\chi_1(\mathbf{q}, t) \sim 1/2Dq^2 \qquad (4.13b)$$

As expected, one finds that $\chi_1 \to 0$ and $\chi_2 \to 0$ as $q \to \infty$. The behavior of χ_1 and χ_2, proportional to $(Dq^2)^{-1}$ as $q \to \infty$, is not unusual in diffusive reactions: another example is the pre-gel solution (3.3b).

4.2. The Limit $q \to 0$

The behavior of $\chi_i(\mathbf{q}, t)$ for $q \to 0$ is of the form

$$\chi_i(\mathbf{q}, t) = \chi_i(\mathbf{0}, t) + \eta_i(t)\, Dq^2 + \cdots \qquad (q \to 0) \tag{4.14}$$

where $\chi_i(\mathbf{0}, t)$ is given in (4.5). Substitution of (4.14) into (4.7) yields three coupled differential equations for the coefficients η_i in (4.14),

$$\dot{\eta}_1(t) = 2(t-1) - 2[1 + (t-1)\, M_2^{(s)}]\, \eta_2 - 2M_2^{(s)}\eta_1 \tag{4.15a}$$

$$\begin{aligned} \dot{\eta}_2(t) = & -1 + (Q_{00} M_2^{(s)}/e_{00})\, \eta_1 \\ & + [(t-1)\, Q_{00}/e_{00} - 1]\, M_2^{(s)}\eta_2 + M_2^{(s)}\eta_3 \end{aligned} \tag{4.15b}$$

$$\dot{\eta}_3(t) = -2(Q_{00}/M_2^{(s)})\, \eta_2 + (2Q_{00}/M_2^{(s)} - Q_{00}/e_{00})\, \eta_3 \tag{4.15c}$$

The equations are to be solved with the initial condition $\eta_i(0) = 0$ $(i = 1, 2, 3)$.

4.3. The Limit $t \to \infty$

To obtain a first impression of the long-time behavior of $\chi_i(\mathbf{q}, t)$, let us take the limit $t \to \infty$ in the results of the previous sections for large and small values of q. I discuss the results for $q \to \infty$ first, and then those for $q \to 0$.

Consider the large-q result (4.12) for $\chi_3(\mathbf{q}, t)$. From the explicit form (1.13) of $c_k(t)$ one can infer that $M_2^{(s)}(t) \sim e^{-t}$ as $t \to \infty$. Similarly, it follows from (4.8) and (4.2c) that $Q_{00}(t) \sim e^{-t}$ and $e_{00}(t) \sim e^{-t}$ as $t \to \infty$. As an immediate consequence, one finds that, for $t \to \infty$, $I_s(t, t')$ increases exponentially as a function of t, i.e.,

$$I_s(t, t') \sim e^t J_s(t') \qquad (t \to \infty) \tag{4.16a}$$

with $J_s(t)$ defined as

$$J_s(t) = 2\frac{Q_{00}(t)}{M_2^{(s)}(t)} \exp\left[-t + \int_t^\infty dt' \left(2\frac{Q_{00}(t')}{M_2^{(s)}(t')} - \frac{Q_{00}(t')}{e_{00}(t')} - 1\right)\right] \tag{4.16b}$$

Note that $J_s(t) \sim 2e^{-t}$ as $t \to \infty$. From (4.12a) and (4.13) it now follows that, in the combined limit, first $q \to \infty$, then $t \to \infty$,

$$\chi_3(\infty, t) \sim \alpha_s e^t \tag{4.17a}$$

$$\chi_2(\mathbf{q}, t) \sim \alpha_s / Dq^2 \qquad (q \to \infty; t \to \infty) \tag{4.17b}$$

$$\chi_1(\mathbf{q}, t) \sim 1/2Dq^2 \tag{4.17c}$$

where the constant α_s is defined as $\alpha_s \equiv \int_0^\infty dt'\, J_s(t')$.

Next consider the small-q results (4.14) and (4.15) in Section 4.2. Formal integration of Eq. (4.15c) yields for the coefficient $\eta_3(t)$ in $\chi_3(\mathbf{q}, t)$

$$\eta_3(t) = -\int_0^t dt'\, \eta_2(t')\, I_s(t, t') \tag{4.18}$$

The large-time behavior of $\eta_3(t)$ is, due to (4.16a), given by

$$\eta_3(t) \sim \beta_s e^t \qquad (t \to \infty) \tag{4.19a}$$

where the constant β_s is defined as

$$\beta_s \equiv -\int_0^\infty dt'\, \eta_2(t')\, J_s(t') \tag{4.19b}$$

This result for $\eta_3(t)$ can now be used to determine the asymptotic behavior of $\eta_1(t)$ and $\eta_2(t)$ as $t \to \infty$. From (4.15a), (4.15b) one readily deduces that

$$\eta_1(t) \sim (2 - \beta_s) t^2 \tag{4.20a}$$

$$(t \to \infty)$$

$$\eta_2(t) \sim (\beta_s - 1) t \tag{4.20b}$$

Note that β_s in (4.19b) converges due to (4.20b).

The previous results, valid for $q \to \infty$ and $q \to 0$, respectively, can now be used to study the large-time behavior of $\chi_i(\mathbf{q}, t)$ at a fixed, positive value of q $(0 < q < \infty)$. I consider $\chi_3(\mathbf{q}, t)$ first, and then χ_2 and χ_1.

I start with the observation that, qualitatively, $\chi_3(\mathbf{q}, t)$ has the same structure at large and at small q, namely

$$\chi_3(\mathbf{q}, t) \sim 1 + \gamma_s(q)\, e^t \qquad (t \to \infty) \tag{4.21a}$$

where $\gamma_s(q) \to \alpha_s$ as $q \to \infty$, and $\gamma_s(q) \sim \beta_s D q^2$ as $q \to 0$. Hence, I take (4.21) as an Ansatz for the large-time behavior for general values of q. Formal integration of (4.7c) shows, with the use of (4.16), that this Ansatz is consistent and, moreover, that $\gamma_s(q)$ can be expressed in terms of $\chi_2(\mathbf{q}, t)$, as follows:

$$\gamma_s(q) = \int_0^\infty dt'\, J_s(t')[1 - \chi_2(\mathbf{q}, t')] \tag{4.21b}$$

The convergence of the integral on the right-hand side imposes a restriction on χ_2 that will be verified below.

Next consider $\chi_2(\mathbf{q}, t)$ and $\chi_1(\mathbf{q}, t)$ as $t \to \infty$. The method used to study the large-time behavior is the same in both cases. We start from (4.7a) or (4.7b), perform a formal integration, and analyze the result for large values of t. For $\chi_2(\mathbf{q}, t)$ one finds that

$$\chi_2(\mathbf{q}, t) \sim 1 + [\gamma_s(q)/Dq^2 - 1](1 - e^{-Dq^2 t}) \qquad (t \to \infty) \tag{4.22}$$

while $\chi_1(\mathbf{q}, t)$ can be expressed in terms of $\chi_2(\mathbf{q}, t)$ as follows:

$$\chi_1(\mathbf{q}, t) \sim \int_0^t dt' \, [1 - 2\chi_2(\mathbf{q}, t')] \, e^{-2Dq^2(t-t')} \qquad (t \to \infty) \tag{4.23}$$

These results are valid for general q values ($0 \leqslant q < \infty$). Note that $\gamma_s(q)$ in (4.21b) converges due to (4.22), and that (4.22) and (4.23) reduce to the results of Sections 4.1 and 4.2 in the limit of large or small q.

Equations (4.23) and (4.22) in combination with (4.21b) are still quite complicated. A limit in which these expressions for χ_1 and χ_2 become very simple is the *combined limit* $t \to \infty$ and $q \to 0$ with the new variable $x \equiv Dq^2 t$ kept fixed. In this limit one finds that

$$\chi_2(\mathbf{q}, t) \to \varphi_2(x) \qquad (x \equiv Dq^2 t) \tag{4.24a}$$

$$\chi_1(\mathbf{q}, t) \to -t\varphi_1(x) \tag{4.24b}$$

where $\varphi_1(x)$ and $\varphi_2(x)$ are given by

$$\varphi_2(x) \equiv \beta_s + (1 - \beta_s) \, e^{-x} \tag{4.24c}$$

$$\varphi_1(x) \equiv x^{-1} \int_0^x dy \, [2\varphi_2(y) - 1] \, e^{2(y-x)} \tag{4.24d}$$

If desired, $\varphi_1(x)$ can easily be calculated explicitly. The physical relevance of the combined limit $t \to \infty$ and $q \to 0$, with $Dq^2 t$ fixed is that small q values, of the order of $(Dt)^{-1/2}$, correspond to *large distances*, with $|\mathbf{r}|$ of the order of $(Dt)^{1/2}$. Such distances are particularly interesting, since $(Dt)^{1/2}$ is the typical distance over which the correlations can spread in time t. Recall that the diffusion constants in (4.7a) and (4.7b) are $2D$ and D, respectively.

The expressions (4.24) for the Fourier transforms $\chi_2(\mathbf{q}, t)$ and $\chi_1(\mathbf{q}, t)$ can readily be inverted with the use of (3.6). The results are respectively given by

$$G_2(\mathbf{r}, t) = \beta_s \delta(\mathbf{r}) + (1 - \beta_s) \, g(\mathbf{r}; 2Dt) \tag{4.25a}$$

$$G_1(\mathbf{r}, t) = -\int_0^t dt' \, [(2\beta_s - 1) \, g(\mathbf{r}; 4D(t - t')) + 2(1 - \beta_s) \, g(\mathbf{r}; 2D(3t - 2t'))] \tag{4.25b}$$

Note that, in this combined limit, $G_2(\mathbf{r}, t)$ and $G_1(\mathbf{r}, t)$ take the form of a superposition of Gaussians. Further note that $G_2(\mathbf{r}, t)\, d\mathbf{r}$ and $t^{-1}G_1(\mathbf{r}, t)\, d\mathbf{r}$ can be expressed in terms of the single new variable $\mathbf{R} \equiv \mathbf{r}/(Dt)^{1/2}$.

4.4. The Limit $s \to \infty$

I comment on the behavior of the fluctuations in the limit $s \to \infty$, where the model (4.1) reduces to the pre-gel model (3.1). As I shall show below, the results are dramatically different in the pre- and in the post-gel stage.

Let us start with the results for $t < t_c = 1$. In this case $M_2^{(s)}(t) \to (1-t)^{-1}$ as $s \to \infty$, due to (3.11), so that Eq. (4.7a) for $\chi_1(\mathbf{q}, t)$ reduces to

$$\dot{\chi}_1(\mathbf{q}, t) = 1 - 2[(1-t)^{-1} + Dq^2]\, \chi_1 \qquad (4.26)$$

The solution is $\chi_1(\mathbf{q}, t) = (1-t)\, \chi(\mathbf{q}, t)$, where $\chi(\mathbf{q}, t)$ is the pre-gel result (3.3b). Comparison of the expressions (4.4a) and (3.3a) for $F_{kl}(\mathbf{q}, t)$ shows that both are identical, i.e., we recover the results of Section 3 if we take the limit $s \to \infty$ in the results of this section. Strictly speaking, this argument is complete only if we show that $\chi_2(\mathbf{q}, t)$ and $\chi_3(\mathbf{q}, t)$ in (4.7) are well behaved as $s \to \infty$. In fact, one can show, with the use of the explicit form (1.13) of $c_k(t)$, that $\chi_2(\mathbf{q}, t) \to \chi(\mathbf{q}, t)$ and $\chi_3(\mathbf{q}, t) \to 1$ if $s \to \infty$. This justifies the derivation of (4.26).

To obtain an impression of the behavior as $s \to \infty$ in the *post-gel stage*, it suffices to consider the gel–gel correlations, represented by $\chi_3(\mathbf{q}, t)$. For simplicity, let us consider only the behavior of χ_3 as $q \to \infty$, which corresponds to correlations at extremely small distances. The large-q behavior of χ_3 is given in (4.12). From (4.8) it follows for all $t > 1$ that $Q_{00}(t) \sim g(t)\, M_3(t)$ as $s \to \infty$, where $g(t)$ is the gel fraction. Furthermore, $M_2^{(s)}(t) \to M_2(t)$ as $s \to \infty$. The behavior of $Q_{00}(t)$ and $M_2(t)$ for $t \downarrow 1$ is given by[16]

$$Q_{00}(t) \sim 2(t-1)^{-2}; \qquad M_2(t) \sim (t-1)^{-1} \qquad (t \downarrow 1) \qquad (4.27)$$

Insertion of (4.27) into (4.12) immediately shows that $\chi_3(\infty, t)$ *diverges* for all $t > 1$ as $s \to \infty$:

$$\chi_3(\infty, t) \geqslant \int_1^t dt'\, I_s(t, t') \to \infty \qquad (s \to \infty) \qquad (4.28)$$

This may be seen from Eq. (4.12b), which implies that $I_s(t, t') \propto (t'-1)^{-4}$ as $t' \downarrow 1$. Hence the integral in (4.28) diverges at its lower boundary. The divergence of the gel–gel fluctuations in (4.28) leads to the same conclusion as was found below Eq. (3.15): for the model (3.1), corresponding to $s=\infty$, the method of this paper breaks down at the gel point t_c. Note, however, that such problems do not occur for any description with $s<\infty$.

4.5. Calculation of d_c

The previous large-time results for the spatial fluctuations in the post-gel stage (Section 4.3) can be used to calculate the upper critical dimension d_c in the model $K_{ij}=ij$, with D_k given by (4.1). The upper critical dimension is the dimension above which a mean-field treatment is allowed, i.e., above which the macroscopic law is correctly given by the rate equations (1.10).

The fundamental equation in the argument is (2.9a), which gives an *exact* description of the time evolution of the averages $\langle m_{k\alpha}(t)\rangle$, with $k=1,\dots,r$. This equation may be written in the form

$$\frac{\partial}{\partial t}\langle m_{k\alpha}\rangle_{\mathrm{R}}=S_k(t)+F_k(t)\qquad (k=1,\dots,r)\tag{4.29}$$

where $S_k(t)$ represents the right-hand side of Eq. (2.11a), and $F_k(t)$ is the correction due to fluctuations:

$$\begin{aligned}F_k(t)=&-(2v)^{-1}\sum_{i,j=1}^{r}K_{ij}(\delta_{ik}+\delta_{jk}-\delta_{i+j,k})[m_{i\alpha}m_{j\alpha}\rangle\!\rangle\\&-v^{-1}k[m_{k\alpha}m_{0\alpha}\rangle\!\rangle\end{aligned}\tag{4.30}$$

The cumulant $[\cdots\rangle\!\rangle$ has been defined in (2.12b).

The mean field assumption is that the contributions F_k in (4.29) due to fluctuations are negligibly small, i.e., that

$$R_k(t)\equiv F_k(t)/S_k(t)\ll 1\tag{4.31}$$

If this condition is fulfilled, then the macroscopic law is given by (2.11a). The condition (4.31) is clearly fulfilled in any dimension at *short* times, because the fast diffusion ($D\gg 1$) smoothes out possible fluctuations. Whether (4.31) is also correct at *large* times depends on the space dimension d. One finds that $R_k(\infty)\ll 1$ above some critical dimension d_c, and $R_k(\infty)=\infty$ if $d\leqslant d_c$. The calculation of d_c is the subject of this section.

To determine the value of d_c, start from the definition (4.31) of R_k and calculate R_k *within the mean field approximation*, assuming that (1.10) holds. As stated above, this is allowed in any dimension at short times, and for all $t>0$ if $d>d_c$. From the explicit form (1.13) of $c_k(t)$ one finds that the large-time behavior of $S_k(t)$ is given by

$$S_k(t)\sim -vkc_k(t)\qquad (t\to\infty)\tag{4.32}$$

Similarly, the dominant terms as $t \to \infty$ in (4.30) follow from (4.4) as

$$F_k(t) \sim -v^{-1}k[m_{k\alpha}m_{0\alpha}\rangle\!\rangle \sim -k\int_v d\mathbf{r}\, E_{k0}(\mathbf{r}, t) \tag{4.33}$$

where the $\mathbf{r}$ integral is calculated over a cell of size v, centered around the origin. Combination of Eqs. (4.33), (4.32), and (4.31) then yields for the large-time behavior of $R_k(t)$

$$\begin{aligned} R_k(t) &\sim v^{-1}\int_v d\mathbf{r}\, E_{k0}(\mathbf{r}, t)/c_k(t) \\ &\sim -v^{-1}k\int_v d\mathbf{r}\, G_2(\mathbf{r}, t) \end{aligned} \tag{4.34}$$

where $G_2(\mathbf{r}, t)$ is the inverse Fourier transform of $\chi_2(\mathbf{q}, t)$ in (4.4b).

The spatial profile $G_2(\mathbf{r}, t)$ of the sol–gel correlations may be determined from Eq. (4.22). From (4.17b) we know that for small distances, or large q values, $\gamma_s(q) \to \alpha_s$, so that $\chi_2(q, t)$ in (4.22) may be written as

$$\chi_2(\mathbf{q}, t) \sim e^{-Dq^2t} + \alpha_s \int_0^t dt'\, e^{-Dq^2t'} \tag{4.35}$$

This equation may readily be inverted to yield

$$G_2(\mathbf{r}, t) \sim g(\mathbf{r}; 2Dt) + \alpha_s \int_0^t dt'\, g(\mathbf{r}; 2Dt') \tag{4.36}$$

where $g(\mathbf{r}; \sigma^2)$ is the d-dimensional Gaussian distribution (3.6a). With the use of (4.36) and (4.34) it is now easy to show that $R_k(t)$ remains finite for all $t > 0$ if $d > 2$:

$$R_k(t) \propto -\alpha_s k v^{(2-d)/d} D^{-1} \qquad (t \to \infty;\, d > 2) \tag{4.37a}$$

while $R_k(t)$ diverges for $d \leqslant 2$:

$$R_k(t) \propto -\alpha_s k D^{-1} \log t \qquad (t \to \infty;\, d = 2) \tag{4.37b}$$

$$R_k(t) \propto -\alpha_s k (t/D)^{1/2} \qquad (t \to \infty;\, d = 1) \tag{4.37c}$$

The unspecified numerical prefactors on the right in (4.37a)–(4.37c) are all of the order of unity.

From (4.37) it immediately follows that the upper critical dimension is $d_c = 2$, since $R_k(t)$ diverges if $d \leqslant 2$ and remains finite (and small) if $d > 2$. The fact that $R_k(\infty)$ is small for $d > 2$ follows from the assumptions $v \gg 1$

and $D \gg 1$. As a remark I add that above d_c was calculated from the kinetic equation (2.9a) for $\langle m_k(t) \rangle$, with $k = 1, \ldots, r$. One could equally well have started from Eq. (2.9b) for the mass $\langle m_0(t) \rangle$, contained in clusters larger than r. In this case one finds of course the same result, $d_c = 2$, independent of the reactant under consideration.

4.6. Conclusions

The main results and conclusions are as follows.

1. The divergence of the density fluctuations at t_c found in Section 3 is an *artefact* of the model (3.1) with $s = \infty$. This divergence does not occur in the model (4.1).

2. Section 4.4, which considered the limit $s \to \infty$, shows that the results for the model (4.1) depend sensitively on the value of s, at least in the post-gel stage. In the pre-gel stage the results are relatively insensitive to the choice of s.

3. A physically interesting limit is the limit $t \to \infty$ and $q \to 0$ with the combination $x = Dq^2t$ fixed. In this case the results are very simple. For $1 \leqslant k$, $l \leqslant s$ one finds that $F_{kl}(\mathbf{q}, t) \to e_{kl}(t)\, \varphi_1(x)$; for $l = 0$ it follows that $F_{k0}(\mathbf{q}, t) \to e_{k0}(t)\, \varphi_2(x)$. The form of $\varphi_1(x)$ and $\varphi_2(x)$ is given in (4.24).

4. The large-time behavior of the *gel–gel correlations* is given by $F_{00}(\mathbf{q}, t) \sim \gamma_s(q)$ as $t \to \infty$. Hence the covariance $E_{00}(\mathbf{r}, t)$ approaches a constant spatial profile at large times. From the fact that $\gamma_s(q) \sim \alpha_s$ as $q \to \infty$ it follows that the variance of the gel mass contained in small subvolumes V_0 is given by $\alpha_s V_0$ at $t \to \infty$. If the gel mass were distributed independently over the subvolumes V_0 according to Poisson statistics, one would find V_0 for the variance. The factor α_s therefore gives the deviation from the Poisson result due to the combined influence of reactions and diffusion. Note that $\alpha_s \to \infty$ as $s \to \infty$.

5. In many results, such as those of conclusion 3 and 4, the s dependence enters only through numerical prefactors like α_s and β_s. Hence, different values of s in (4.1) lead to a different *magnitude* of the fluctuations, and not to qualitatively different behavior. Recall that α_s and β_s become large for large values of s.

6. In Section 4.5 it was shown that the upper critical dimension in this model is $d_c = 2$. However, from (4.37b) and (4.37c) it follows that the mean field assumption (4.31) is correct also *below* the upper critical dimension (i.e., for $d \leqslant 2$), provided that one restricts oneself to times that are not too large: $t \lesssim t_D$, where $t_D = \exp(D/k\alpha_s)$ if $d = 2$, and $t_D = D/(k\alpha_s)^2$ if $d = 1$. Since it was assumed that the aggregation process is reaction limited

$(D \gg 1)$, it can be inferred that the mean field results are also applicable in $d=2$ for any practical purpose, and in $d=1$ at least for a considerable time interval.

7. On the other hand, it is also manifest in (4.37a) that the fluctuations may become large even for $d>2$: (i) if α_s is large (which happens if large clusters are very mobile: $s \gg 1$); (ii) if the cluster size k is large; in this case the fluctuations become large because of the large reactivity (short lifetime) of a k-mer; (iii) if the diffusion constant D is small, which corresponds to diffusion-limited aggregation. This limit is not considered in this paper.

5. DISCUSSION

In this paper I studied the spatial fluctuations in coagulating systems with *rate constants* $K_{ij}=ij$ and *diffusion constants* D_k. The starting point was a master equation for a cell model, where clusters react within each cell, and jump between cells. From the master equation I derived approximate kinetic equations for the average occupation numbers (concentrations) and for the fluctuations about those averages (equal-time and two-time correlation functions). The basic assumption underlying the derivation of these equations is that clusters diffuse over large distances (much larger than the cell diameter) before they finally react. In this case one can apply the Ω-expansion within each cell, assuming that the cells are large (i.e., contain many clusters). Furthermore, one can transform from the cell picture to a continuum formulation, replacing the jump constants by a diffusion operator.

I start the discussion with some comments on the *method* of this paper. For this purpose I focus on the basic assumption, that clusters diffuse over large distances before they finally react. The average (RMS) distance $l(k)$ traveled by a k-mer during its lifetime is given by

$$l(k) = (2D_k \tau_k)^{1/2} \tag{5.1}$$

where D_k is the diffusion coefficient of a k-mer and τ_k is its average lifetime. In reaction–diffusion processes, the distance $l=(2D\tau)^{1/2}$ defines an important length scale.(20) It is known as the *Kuramoto length.*(5) From (5.1) it follows immediately that our basic approximation, that $l(k)$ is large compared to the cell size, cannot be correct for very large clusters, since $l(k)$ vanishes as $k \to \infty$. *Two effects* tend to decrease $l(k)$. First, in physical systems one expects that $D_k \to 0$ as $k \to \infty$. Second, for the rate constants $K_{ij}=ij$ considered in this paper, one has $\tau_k \to 0$ as $k \to \infty$. The latter fact may not be so obvious, and will be discussed next.

To calculate τ_k, consider a cluster of size k, brought into the system at some time $t_0 \geqslant 0$. The probability that the k-mer has not yet reacted at the (later) time $t > t_0$ is denoted by $P_k(t)$. For a spatially uniform initial distribution, this probability satisfies a simple master equation. The transition rates for a reaction in cell α are

$$T_k(t) = v^{-1} \sum_j K_{kj}(m_{j\alpha} - \delta_{kj}) \tag{5.2}$$

or, to leading order in the cell size v, $T_k(t) = k$. I used that, on the average, the mass density is equal to unity for all $t > 0$. The master equation for $P_k(t)$ is

$$\dot{P}_k(t) = -kP_k(t) \tag{5.3}$$

The solution has the form $P_k(t) = \exp[-k(t - t_0)]$ (all $t > t_0$). As a consequence, one finds that τ_k is, for all times $t_0 \geqslant 0$, given by

$$\tau_k = \int_{t_0}^{\infty} dt\, (t - t_0)\, \dot{P}_k(t) = 1/k \tag{5.4}$$

Hence τ_k vanishes as $k \to \infty$. Clearly, the physical explanation is that large clusters are very reactive, implying that their average lifetime is very short.

The Kuramoto length now follows from (5.1) and (5.4) as $l(k) = (2D_k/k)^{1/2}$. From the fact that $l(k) \to 0$ as $k \to \infty$, I conclude that this method is inaccurate for clusters with a Kuramoto length smaller than the cell diameter: $k \gtrsim k_D$, with $l(k_D) \equiv v^{1/d}$. Fortunately, the contributions of such large clusters to the rate equations for the smaller clusters ($k \ll k_D$) are *exponentially small*, of the order of $c_{k_D}(t)$. Hence I conclude that, although large clusters are treated inaccurately in this method, the resulting error in the quantities of interest is negligibly small.

Next I comment on the exactly soluble models discussed in Sections 3 and 4. The diffusion constants corresponding to these models are $D_k = D$ ($k = 1, 2,\ldots$) and $D_k = D$ ($1 \leqslant k \leqslant s$), $D_k = 0$ ($k > s$), respectively. On one hand, these models are complementary, since large clusters are extremely mobile in the former and completely immobile in the latter model. On the other hand, the model of Section 4 reduces to that of Section 3 in the limit $s \to \infty$. Combination of both models thus yields some insight into the possible behavior of the spatial fluctuations in (reaction-limited) aggregation processes.

In the model $D_k = D$ ($k = 1, 2,\ldots$), large clusters are clearly much too mobile. The large mobility of large clusters is unimportant at short times, since in this case large clusters are scarce. Artefacts are to be expected only in the vicinity of the gel point. Examples of such artefacts are the *divergence* of the density fluctuations at $t \to t_c$ and the *vanishing width* of the spatial profile $G(\mathbf{r}, t)$ in (3.7b). These results are not realistic: in the models of Section 4 one does not find a divergence of the fluctuations or a contraction to a delta peak. Nevertheless, the model (3.1) reveals very clearly and explicitly the tendencies present also in the model (4.1). For this reason I consider the results of the model (3.1) in some more detail.

One of the more remarkable features of the model (3.1) is that the spatial profile of the fluctuations contracts to a delta function: $G(\mathbf{r}, t) \to \delta(\mathbf{r})$ as $t \to t_c$. In reaction–diffusion systems one would expect that the correlations spread out, i.e., that the width of $G(\mathbf{r}, t)$ increases, rather than decreases, in the course of time. The explanation of this paradox lies in the definition of the *width* of a distribution. Many different definitions are possible, and, as I shall show, lead to different results. For definiteness, define the width of $G(\mathbf{r}, t)$ as

$$\langle r \rangle_\alpha \equiv \int d\mathbf{r}\, |\mathbf{r}|^{\alpha+1}\, G(\mathbf{r}, t) \bigg/ \int d\mathbf{r}\, |\mathbf{r}|^{\alpha}\, G(\mathbf{r}, t) \tag{5.5}$$

and consider the behavior of $\langle r \rangle_\alpha$ for various choices of the parameter α. Note that correlations at large distances are emphasized if the value of α is large. The use of Eq. (3.7b) for $G(\mathbf{r}, t)$ leads to the following results. The physically expected behavior, where $\langle r \rangle_\alpha$ increases as a function of time, is obtained if one chooses $\alpha > 2$. In this case the value of $\langle r \rangle_\alpha$ at t_c is finite, of the order of $(Dt_c)^{1/2}$. For $\alpha \leqslant 2$ one finds that $\langle r \rangle_\alpha \to 0$ as $t \to t_c$. Thus, one arrives at the following physical picture. If one concentrates on large distances and chooses a large value of α (i.e., $\alpha > 2$), then the correlations spread out, as expected, with a diffusion constant $2D$. However, if one chooses $\alpha \leqslant 2$, one emphasizes the short-range correlations whose amplitude *diverges* as $t \to t_c$.

Now consider a second remarkable result of the model (3.1), namely the divergence of the density fluctuations at the gel point t_c; I address two questions: (1) how can this divergence be understood intuitively, and (2) does it occur also for other models? The answer to the first question is simply that, due to their large mobility, large clusters contribute significantly to the fluctuations in the density. This effect becomes important in the vicinity of the gel point, where the number of large clusters is large. The answer to the second question is more technical, and will be discussed next.

Consider in general a model with diffusion constants D_k. An equation for the (Fourier-transformed) density–density correlation function $\hat{\rho}(\mathbf{q}, t)$ can be obtained by multiplying Eq. (3.2a) with kl and summing over all k and l. The result is

$$\frac{\partial}{\partial t} \hat{\rho}(\mathbf{q}, t) = -2q^2 \sum_{i,j} ij D_i F_{ij}(\mathbf{q}, t) \tag{5.6}$$

Note that Eq. (5.6) is not a closed equation for $\hat{\rho}(\mathbf{q}, t)$ and that $F_{ij}(\mathbf{q}, t)$ is not known exactly. However, we are interested only in the behavior of $\hat{\rho}(\mathbf{q}, t)$ as $t \uparrow t_c$. For this purpose it is possible to argue as follows. Assume that, for some $\beta > 0$, $D_k \sim Dk^{-\beta}$ as $k \to \infty$. For the model $D_k = D$ it is found (see the Appendix) that $F_{ij}(\mathbf{q}, t)$ approaches a scaling form as $t \uparrow t_c$, independent of the details of the initial distribution. More precisely: in the scaling limit, $F_{ij}(\mathbf{q}, t) \to e_{ij}(t)$, where $e_{ij}(t)$ is the factorial cumulant of the nonspatial problem. Note that the *same* scaling form leads to a consistent solution of Eq. (3.2) for *general* choices of D_k. Replacing $F_{ij}(\mathbf{q}, t)$ on the right-hand side of (5.6) by $e_{ij}(t)$ and approximating the sums by integrals shows that in the vicinity of t_c

$$\frac{\partial}{\partial t}\hat{\rho}(\mathbf{q}, t) \propto Dq^2(t_c - t)^{2\beta - 1} \qquad (t \uparrow t_c; \beta < \tfrac{1}{2}) \tag{5.7}$$

while $\partial\hat{\rho}/\partial t \to \text{const}$ if $\beta > 1/2$. The prefactor on the right in (5.7) is positive and of the order of unity. It follows immediately from (5.7) that the density correlations remain finite for all $\beta > 0$. For $\beta = 0$ one finds that $\hat{\rho}(\mathbf{q}, t)$ diverges as $t \uparrow t_c$, proportional to $|\ln(t_c - t)|$, in agreement with (3.15).

Another interesting feature of both the model (3.1) and the models of Section 4 is the role played by the *Kuramoto length.* In the literature(5,20) the distance l traveled by a particle during its lifetime is identified as a statistically important length scale: in volumes much *smaller* than l^d the fluctuations in the cluster size distribution obey Poisson statistics. On the other hand, if one considers a subsystem much *larger* than l^d, the fluctuations are the same as for the well-stirred case. The results in this paper are somewhat different. In Section 3 it was found that, although each cluster size k has a different Kuramoto length $l(k)$, defined in (5.1), there is, for all cluster sizes k, only *one length* that determines the boundary line between Poisson and well-stirred statistics. This length, denoted by $\bar{l}$, is the "width" of the function $G(\mathbf{r}, t)$ in (3.7b), where in this case "width" should be defined by

$$\int_{|\mathbf{r}| \leqslant \bar{l}} G(\mathbf{r}, t)\, d\mathbf{r} \equiv \tfrac{1}{2} \tag{5.8}$$

Similarly, it was found in Section 4 that the spatial profile of the factorial cumulants $E_{kl}(\mathbf{r}, t)$ is described by a *single* function $G_1(\mathbf{r}, t)$ if we restrict ourselves to cluster sizes satisfying $1 \leqslant k,\ l \leqslant s$. I conclude that, in the present models, the statistics for a particular species is not determined by the Kuramoto length of that species, but rather by some "average" Kuramoto length in the system.

Next I comment on the significance of the nonspatial model(17,21) for reaction–diffusion systems. In the nonspatial (or single-cell) model it is assumed that all pairs of i- and j-mers are equally likely to form a bond. The usual interpretation(5,6) is that either the system is "well-mixed" or diffusion occurs so fast that the clusters are able to traverse the entire system before they finally react. In reaction–diffusion systems of macroscopic size these possibilities are both somewhat unrealistic: diffusion is usually not that fast, and mixing with microscopic finesse would be more than miraculous. Here I want to point out that the results from the nonspatial model have in fact *great significance* for the reaction–diffusion problem, but for a different reason. This reason is that the nonspatial correlation functions occur in the reaction–diffusion problem as *integrals* over the (spatial) correlation functions, at least if the initial state of the system is spatially uniform. This fact is expressed by Eqs. (2.45) and (2.46) for the equal-time and the two-time correlation functions, respectively. This conclusion is of course also true in general for any related reaction–diffusion problem.

The new interpretation of the nonspatial results suggests a relatively simple way in which the present theory could be verified experimentally. The integrated (or nonspatial) correlation functions are in principle accessible in computer simulations. Hence one could try to extend the nonspatial fluctuation theory(17,21) to other fields, e.g., to percolation,(22) or to test it in simulations of cluster–cluster aggregation processes.(23) From a physical point of view, the outcome of such experiments would be very interesting. Similar remarks were made already in ref. 21.

In this paper it is assumed throughout that the initial state of the system is *spatially uniform.* Here I comment on the possible influence of inhomogeneities in the initial state. First, if the inhomogeneities are *large* (of macroscopic size), one expects that they will partly fade out in the course of time due to diffusion, but some reminiscences of the initial state will always be present near the gel point. This then leads to a spatial variation of the gel time $t_c(\mathbf{r})$ that will also be of influence on the final state of the system ($t = \infty$).

Second, I discuss the important case where the inhomogeneities are *small,* of relative order $v^{-1/2}$ in each cell of size v. In the notation of Section 2.1 this means that

$$m_{k\alpha}(0) = vc_k(0) + v^{1/2}\xi_{k\alpha}(0) \tag{5.9a}$$

where $\xi_{k\alpha}(0)$ is of the order of unity. This is precisely what one would expect for the spontaneous statistical fluctuations in the initial state, which are described by a multinomial (or, since v is small, Poisson) distribution.

In this case one finds that the average number of k-mers in cell α takes the form

$$\langle m_{k\alpha}(t)\rangle = vc_k(t) + v^{1/2}\langle \xi_{k\alpha}(t)\rangle \tag{5.9b}$$

where $\langle \xi_{k\alpha}\rangle$ satisfies the same linearized kinetic equation (2.18), (2.22) as $\overline{\Delta m_{k\alpha}}$. Equation (5.9b) has the following consequences:

(i) To dominant order in the Ω-expansion one finds that $\langle m_{k\alpha}(t)\rangle = vc_k(t)$, so that the macroscopic law is still given by (1.10).

(ii) The kinetic equations for the equal-time and two-time correlation functions are still given by (2.37), (2.40).

(iii) The initial conditions, too, are the same as for the spatially uniform case.

From this one can conclude that *all results of this paper are valid also if the initial state contains statistical fluctuations, as in (5.9a).*

An extension of this paper in a different direction has already proved possible. Here I considered only one special choice for the rate constants, namely $K_{ij} = ij$. However, the method discussed in Section 2 is quite general and can also be applied for different choices for K_{ij}. I have found two other exactly soluble models, corresponding to the nongelling models $K_{ij} = 1$ and $K_{ij} = i + j$. Furthermore, I have obtained some qualitative results, including a scaling theory, for rate constants that are homogeneous functions of the cluster sizes i and j. These results for other models will be published elsewhere.[5]

Finally, I highlight the main results. In this paper I presented a new kinetic model, describing reaction-limited aggregation, in which the spatial fluctuations can be calculated explicitly. The model under consideration is of special interest since it describes a phase transition (gelation), and the fluctuations can be studied in detail, both in the pre- and in the post-gel stage. Starting from the master equation (2.4), I showed that the macroscopic law is given by (1.8) for all $t > 0$, and I derived kinetic equations for the equal-time and two-time correlation functions. These equations simplify drastically for spatially uniform initial states: in this case the macroscopic law is Smoluchowski's equation (1.10), and the correlation functions depend only on the distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$.

I considered two exactly soluble models. For the first model ($D_k = D$ for all k), I calculated the two-time correlation functions for monodisperse initial conditions and the equal-time correlation functions for general initial conditions. The large mobility of large clusters leads to a divergence of the density fluctuations at the gel point t_c, implying that, at t_c, the method breaks down. In the second model, large clusters are immobile: $D_k = D$

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[5] See ref. 24 for the results for $K_{ij} = 1$ and for homogeneous rate constants.

($k=1, 2,\ldots, s$), $D_k=0$ ($k>s$). I calculated the equal-time correlation functions for monodisperse initial conditions and found the following results. In this model the density fluctuations are finite at all times, in particular at the gel point t_c. The fluctuations in the post-gel stage depend sensitively on the choice of the diffusion constants, i.e., on the value of s. The explanation is that a large contribution to the fluctuations for $t>t_c$ comes from the neighborhood of the phase transition ($t \simeq t_c$), where the number of large clusters is large. One further finds that the correlation functions assume a very simple form in the physically interesting limit $t \to \infty$ and the distance $|\mathbf{r}| \to \infty$ with the ratio $\mathbf{r}^2/Dt$ fixed. From the large-time results it follows that the upper critical dimension in this gelling model is $d_c=2$.

APPENDIX A

This appendix is devoted to the behavior of the factorial cumulants $E_{kl}(\mathbf{r}, t)$ in (2.37) for general initial conditions $E_{kl}(\mathbf{r}, 0)= -\delta_{kl} c_k(0)\,\delta(\mathbf{r})$. First, in Section A.1, I give the exact solution of Eq. (3.2) for the Fourier transform $F_{kl}(\mathbf{q}, t)$ of $E_{kl}(\mathbf{r}, t)$. The result is formulated in terms of the generating function of $F_{kl}(\mathbf{q}, t)$. Next, in Section A.2, I give an explicit result for $E_{kl}(\mathbf{r}, t)$ for the special case of monodisperse initial conditions, i.e., $c_k(0)=\delta_{k1}$. For general (nonmonodisperse) initial distributions, the generating function results are too complicated to yield *explicit* expressions for $E_{kl}(\mathbf{r}, t)$. However, one can calculate *asymptotic* expressions, valid at large cluster sizes ($k, l \to \infty$), and in the scaling limit. These asymptotic results for $E_{kl}(\mathbf{r}, t)$ are given in Section A.3.

The properties of the fluctuations can be calculated only after the macroscopic law has been solved. This is obvious from Eq. (3.2) for $F_{kl}(\mathbf{q}, t)$, where the concentrations $c_k(t)$ enter both in the linear and in the inhomogeneous part. For this reason I recall some of the most important properties of $c_k(t)$. The macroscopic law (1.10) may be solved in terms of the generating function $f(x, t)$ of $c_k(t)$, which is defined as

$$f(x, t) \equiv \sum_{k=1}^{\infty} k c_k(t)\, e^{kx} \tag{A.1}$$

Substitution of (A.1) into (1.10) shows that $f(x, t)$ satisfies a partial differential equation,

$$\frac{\partial f}{\partial t} + (1-f)\frac{\partial f}{\partial x} = 0 \tag{A.2}$$

which may be solved with the use of the method of characteristics. The result is

$$f(x, t) = u(x_0) \tag{A.3a}$$

where

$$u(x) \equiv f(x, 0) = \sum_{k=1}^{\infty} kc_k(0)\, e^{kx} \tag{A.3b}$$

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

$$x_0(x, t) \equiv x + tf(x, t) - t \tag{A.3c}$$

Below, we need also an expression for the partial derivative of $f(x, t)$ with respect to x:

$$\frac{\partial f}{\partial x}(x, t) = \frac{u'(x_0)}{1 - tu'(x_0)} \tag{A.4}$$

More details concerning $c_k(t)$, or $f(x, t)$, can be found in refs. 15 and 16 or in Appendix B of ref. 17.

A.1. Solution of (3.2) for General Initial Conditions

I shall solve Eq. (3.2) for $F_{kl}(\mathbf{q}, t)$ in terms of the generating function $H(x, y; \mathbf{q}, t)$, which is defined as

$$H(x, y; \mathbf{q}, t) \equiv \sum_{k,l} klF_{kl}(\mathbf{q}, t)(e^{kx} - 1)(e^{ly} - 1) \tag{A.5}$$

Once $H(x, y; \mathbf{q}, t)$ is known, $F_{kl}(\mathbf{q}, t)$ may be calculated by inversion of (A.5). Formally, $F_{kl}(\mathbf{q}, t)$ may be written as a double contour integral in the complex plane[6]:

$$klF_{kl}(\mathbf{q}, t) = \left(\frac{1}{2\pi i}\right)^2 \oint \frac{dw_1}{w_1^{k+1}} \oint \frac{dw_2}{w_2^{l+1}} H(x, y; \mathbf{q}, t) \tag{A.6}$$

where $w_1 \equiv e^x$ and $w_2 \equiv e^y$. The integration paths in (A.6) are closed contours, circling the origins of the complex w_1 and w_2 planes once in the counterclockwise direction. The factorial cumulants $E_{kl}(\mathbf{r}, t)$ may then be calculated by inverse Fourier transformation of (A.6).

To obtain an equation for the generating function H in (A.5), multiply (3.2) with $kl(e^{kx} - 1)(e^{ly} - 1)$, and sum over all k and l. As the result, one finds that H satisfies the following linear partial differential equation:

$$\begin{aligned} &\frac{\partial H}{\partial t} + [1 - f(x, t)]\frac{\partial H}{\partial x} + [1 - f(y, t)]\frac{\partial H}{\partial y} \\ &\quad = -\left[\frac{\partial f}{\partial x}(x, t) - M_2\right]\left[\frac{\partial f}{\partial y}(y, t) - M_2\right] \\ &\qquad + \left[\frac{\partial f}{\partial x}(x, t) + \frac{\partial f}{\partial y}(y, t) - 2Dq^2\right] H \end{aligned} \tag{A.7a}$$

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[6] Throughout this appendix, i stands for the imaginary number $\sqrt{-1}$.

where $M_2(t) = \sum_k k^2 c_k(t)$ is the second moment of $c_k(t)$, and $f(x, t)$ is defined in (A.1). The initial condition for (A.7a) follows from (2.42b), (A.3b), and (A.5) as

$$H(x, y; \mathbf{q}, 0) = u'(x) + u'(y) - u'(x+y) - u'(0) \tag{A.7b}$$

Note that, as a consequence of (A.7b), the boundary condition $H = 0$ at $x = 0$ or $y = 0$ is automatically fulfilled for all $t < t_c$.

In order to solve Eq. (A.7), transform (for a fixed value of $\mathbf{q}$) from the old variables (x, y, t) to new variables (z_1, z_2, t) defined as

$$z_1 \equiv f(x, t); \qquad z_2 \equiv f(y, t) \tag{A.8a}$$

The function H expressed in terms of these new variables, will be denoted as W, i.e.,

$$W(z_1, z_2; \mathbf{q}, t) \equiv H(x, y; \mathbf{q}, t) \tag{A.8b}$$

For W, one finds a relatively simple differential equation if one uses Eq. (A.2) for $f(x, t)$, namely

$$\begin{aligned} \frac{\partial W}{\partial t} = &- \left(\frac{\partial f}{\partial x}(x, t) - M_2 \right) \left(\frac{\partial f}{\partial y}(y, t) - M_2 \right) \\ &+ \left(\frac{\partial f}{\partial x}(x, t) + \frac{\partial f}{\partial y}(y, t) - 2Dq^2 \right) W \end{aligned} \tag{A.9}$$

The relation between $\partial f/\partial x$ (or $\partial f/\partial y$) and the new variables (z_1, z_2, t) follows from (A.4), with x_0 (or y_0) given by (A.3a), i.e.,

$$u(x_0) = z_1; \qquad u(y_0) = z_2 \tag{A.10}$$

Note that $\partial f/\partial x$ and $\partial f/\partial y$ depend only on z_1 and z_2, and not explicitly on t. The initial condition for (A.9) is

$$\begin{aligned} W(z_1, z_2; \mathbf{q}, 0) &= H(x_0, y_0; \mathbf{q}, 0) \\ &= u'(x_0) + u'(y_0) - u'(x_0 + y_0) - u'(0) \end{aligned} \tag{A.11}$$

as follows immediately from (A.8b), (A.10), and (A.7b).

Equation (A.9), with $\partial f/\partial x$ and $\partial f/\partial y$ given by (A.4), may readily be integrated. The result is

$$\begin{aligned} &W(z_1, z_2; \mathbf{q}, t) \\ &\quad = \{[1 - tu'(x_0)][1 - tu'(y_0)]\}^{-1} \Big\{ W(z_1, z_2; \mathbf{q}, 0)\, e^{-2Dq^2 t} \\ &\qquad - [1 - t_c u'(x_0)][1 - t_c u'(y_0)] \int_0^t d\tau\, (t_c - \tau)^{-2}\, e^{-2Dq^2(t-\tau)} \Big\} \end{aligned} \tag{A.12}$$

where x_0 is given by (A.10), and the gel time $t_c = 1/u'(0)$. In combination with the initial condition (A.11), this gives an *exact expression* for $W(z_1, z_2; \mathbf{q}, t)$ and hence, due to (A.8b), for the generating function H in (A.5).

A.2. Monodisperse Initial Conditions

The generating function $W(z_1, z_2; \mathbf{q}, t)$ in (A.12) assumes a particularly simple form if the initial distribution is monodisperse, i.e., if $c_k(0) = \delta_{k1}$. In this case it follows from (A.11), in combination with (A.3b) and (A.10), that

$$W(z_1, z_2; \mathbf{q}, 0) = -(z_1 - 1)(z_2 - 1) \tag{A.13}$$

Insertion of (A.13) into (A.12), where $t_c = 1$ for monodisperse initial conditions, shows that W takes the form

$$W(z_1, z_2; \mathbf{q}, t) = -(1-t)^{-1} \frac{(z_1 - 1)(z_2 - 1)}{(1 - tz_1)(1 - tz_2)} \chi(\mathbf{q}, t) \tag{A.14a}$$

with $\chi(\mathbf{q}, t)$ defined as

$$\chi(\mathbf{q}, t) \equiv (1-t)\, e^{-2Dq^2 t} \left[1 + \int_0^t d\tau\, (1-\tau)^{-2}\, e^{2Dq^2\tau} \right] \tag{A.14b}$$

Insertion of (A.14a) into (A.6) immediately shows that the $\mathbf{q}$ dependence of $F_{kl}(\mathbf{q}, t)$ is completely contained in $\chi(\mathbf{q}, t)$. Furthermore, since $\chi(\mathbf{0}, t) = 1$, it follows from (2.45a) that $F_{kl}(\mathbf{q}, t)$ must have the form

$$F_{kl}(\mathbf{q}, t) = e_{kl}(t)\, \chi(\mathbf{q}, t) \tag{A.15}$$

where $e_{kl}(t)$ is the factorial cumulant (3.3c) of the nonspatial problem. It may readily be verified from (A.14) and (A.6), or simply by inserting (A.15) into (A.5), that $F_{kl}(\mathbf{q}, t)$ in (A.15) indeed leads to the form (A.14) for $W(z_1, z_2; \mathbf{q}, t)$. Note that Eq. (A.15), which has been derived constructively here, is identical to the previous result (3.3).

A.3. General Initial Conditions

For general initial conditions, the result (A.12) for $W(z_1, z_2; \mathbf{q}, t)$ cannot be inverted exactly. Nevertheless, one can obtain simple asymptotic results for $E_{kl}(\mathbf{r}, t)$ in various limits. Below, I consider first the limit of large cluster sizes ($k, l \to \infty$), and then the scaling limit.

Before deriving these asymptotic results, however, I consider Eq. (A.12) for $W(z_1, z_2; \mathbf{q}, t)$ in some more detail. Even if this result for the generating function cannot be inverted explicitly, it follows from (A.12) that the *structure* of $F_{kl}(\mathbf{q}, t)$ is given by

$$F_{kl}(\mathbf{q}, t) = \alpha_{kl}(t)\, e^{-2Dq^2 t} + \beta_{kl}(t) \int_0^t d\tau\, (t_c - \tau)^{-2}\, e^{-2Dq^2(t-\tau)} \tag{A.16}$$

where α_{kl} and β_{kl} can be represented as complex contour integrals due to (A.6). Inverse Fourier transformation of (A.16) then shows that $E_{kl}(\mathbf{r}, t)$ is a superposition of Gaussian distributions $g(\mathbf{r}; \sigma^2)$ also for *general* initial conditions:

$$\begin{aligned} E_{kl}(\mathbf{r}, t) &= \alpha_{kl}(t)\, g(\mathbf{r}; 4Dt) \\ &\quad + \beta_{kl}(t) \int_0^t d\tau\, (t_c - \tau)^{-2}\, g(\mathbf{r}; 4D(t-\tau)) \end{aligned} \tag{A.17}$$

The interpretation of Eq. (A.17) is the same as that of Eq. (3.7b) for monodisperse initial conditions. The first term represents correlations, already present in the initial distribution, that have been spreading during a time t, with diffusion constant $2D$. The second term represents correlations, induced by the reactions at time τ, that have been spreading during the remaining time $(t - \tau)$. This shows that the spatial behavior for general and for monodisperse initial conditions is very similar.

To study the (explicit) asymptotic behavior of $E_{kl}(\mathbf{r}, t)$ at large cluster sizes, it is convenient to rewrite Eq. (A.8), (A.12) as follows:

$$H(x, y; \mathbf{q}, t) = a(x_0, y_0; \mathbf{q}, t) \left(\frac{\partial f}{\partial x}(x, t) - M_2 \right) \left(\frac{\partial f}{\partial y}(y, t) - M_2 \right) \tag{A.18a}$$

where $x_0(x, t)$ is given in (A.3b), and $a(x, y; \mathbf{q}, t)$ is defined as

$$\begin{aligned} a(x, y; \mathbf{q}, t) \equiv \frac{1 - tu'(0)}{u'(x) - u'(0)} \frac{1 - tu'(0)}{u'(y) - u'(0)} \Big\{ & H(x, y; \mathbf{q}, 0)\, e^{-2Dq^2 t} \\ & - [1 - t_c u'(x)][1 - t_c u'(y)] \int_0^t d\tau\, (t_c - \tau)^{-2}\, e^{-2Dq^2(t-\tau)} \Big\} \end{aligned} \tag{A.18b}$$

In the derivation of (A.18) I used the relation (A.4) between $\partial f/\partial x$ and $x_0(x, t)$. The initial value $H(x, y; \mathbf{q}, 0)$ is given in (A.7b).

The asymptotic behavior of $E_{kl}(\mathbf{r}, t)$ as $k \to \infty$ and $l \to \infty$ may now be calculated along the lines of ref. 17, Section 4(ii). For the details see that paper. The method for studying the behavior at large cluster sizes is the *saddle point method.* From ref. 17 one knows that the integrand in (A.6) has a saddle point at the point $x = y = x_s(t)$, with $x_s(t)$ defined by

$$x_s(t) \equiv x_0^s - tu(x_0^s) + t \tag{A.19a}$$

$$u'(x_0^s) \equiv t^{-1} \tag{A.19b}$$

For large values of k and l, only (x, y) values close to this saddle point contribute to the integral in (A.6), implying that

$$\begin{aligned} klF_{kl}(\mathbf{q}, t) &\sim a(x_0^s, x_0^s; \mathbf{q}, t) \left(\frac{1}{2\pi i}\right)^2 \\ &\quad \times \oint \frac{dw_1}{w_1^{k+1}} \oint \frac{dw_2}{w_2^{l+1}} \frac{\partial f}{\partial x}(x, t) \frac{\partial f}{\partial y}(y, t) \\ &\sim a(x_0^s, x_0^s; \mathbf{q}, t)(kl)^2\, c_k(t)\, c_l(t) \qquad (k, l \to \infty) \end{aligned} \tag{A.20}$$

This result may readily be inverted to yield an asymptotic form for $E_{kl}(\mathbf{r}, t)$:

$$E_{kl}(\mathbf{r}, t) \sim \alpha(\mathbf{r}, t)\, klc_k(t)\, c_l(t) \qquad (k, l \to \infty) \tag{A.21a}$$

where $\alpha(\mathbf{r}, t)$ follows from (A.18b), (A.19b), and (A.20) as

$$\begin{aligned} \alpha(\mathbf{r}, t) &= t^2[2t^{-1} - u'(2x_0^s) - t_c^{-1}]\, g(\mathbf{r}; 4Dt) \\ &\quad - (t_c - t)^2 \int_0^t d\tau\, (t_c - \tau)^{-2} g(\mathbf{r}; 4D(t - \tau)) \end{aligned} \tag{A.21b}$$

Thus, at large cluster sizes the $\mathbf{r}$ and (k, l) dependences of $E_{kl}(\mathbf{r}, t)$ factorize. The spatial dependence $\alpha(\mathbf{r}, t)$ in (A.21b) has the form of a superposition of Gaussians. The factor $klc_k(t)\, c_l(t)$ in (A.21a) represents the nonspatial factorial cumulants $e_{kl}(t)$ [see Eq. (4.14) of ref. 17].

Next I consider $E_{kl}(\mathbf{r}, t)$ in the scaling limit (S), which is the limit where $k, l \to \infty$, and the average cluster size $s(t) \to \infty$, with $k/s(t)$ and $l/s(t)$ fixed. The average cluster size is chosen as $s(t) = M_3(t)/M_2(t)$, where $M_n(t)$ is the nth moment of $c_k(t)$, defined in (1.12). The present calculations are completely analogous to those in Section 4(iii) of ref. 17.

We start from $H(x, y; \mathbf{q}, t)$ in the form (A.18), and focus on the factor $a(x_0, y_0; \mathbf{q}, t)$ in (A.18a). From ref. 17 one knows that $x_0(x, t)$ vanishes in the scaling limit, proportional to $-s(t)^{-1/2}$, and similarly

$y_0 \propto -s(t)^{-1/2} \to 0$. As a consequence, one may expand $a(x_0, y_0; \mathbf{q}, t)$ in (A.18b) about $x = y = 0$; one finds that, in the scaling limit,

$$a(x_0, y_0; \mathbf{q}, t) \xrightarrow{\mathrm{S}} -\left(\frac{1 - tu'(0)}{u''(0)}\right)^2 \left[u'''(0)\, e^{-2Dq^2 t} + \left(\frac{u''(0)}{u'(0)}\right)^2 \int_0^t d\tau\, (t_c - \tau)^{-2}\, e^{-2Dq^2(t-\tau)}\right] \tag{A.22}$$

This result can be simplified further. In the scaling limit, where $t \uparrow t_c$, the second term in $[\cdots]$ diverges, so that the first term, proportional to $\exp(-2Dq^2 t)$, can be neglected. Furthermore, the main contribution to the second term comes from the region $\tau \simeq t$, so that the factor $\exp[-2Dq^2(t-\tau)]$ can be replaced by unity as $t \uparrow t_c$. Thus, we find the remarkably simple result that

$$a(x_0, y_0; \mathbf{q}, t) \xrightarrow{\mathrm{S}} -(t_c - t) \tag{A.23}$$

i.e., in the scaling limit $a(x_0, y_0; \mathbf{q}, t)$ becomes independent of the variables x, y, and $\mathbf{q}$.

As a consequence of (A.23), it follows from (A.18a) that

$$H(x, y; \mathbf{q}, t) \xrightarrow{\mathrm{S}} -(t_c - t)\left(\frac{\partial f}{\partial x}(x, t) - M_2\right)\left(\frac{\partial f}{\partial y}(y, t) - M_2\right) \tag{A.24}$$

and, hence, from (A.6) that

$$F_{kl}(\mathbf{q}, t) \xrightarrow{\mathrm{S}} -(t_c - t)\, kl c_k(t)\, c_l(t) \tag{A.25}$$

Comparison of Eq. (A.25) with the scaling form (4.19) in ref. 17 for $e_{kl}(t)$ shows that the right-hand side of (A.25) is *identical* to $e_{kl}(t)$. Hence, Eq. (A.25) may alternatively be written as

$$F_{kl}(\mathbf{q}, t) \xrightarrow{\mathrm{S}} e_{kl}(t) \tag{A.26a}$$

or

$$E_{kl}(\mathbf{r}, t) \xrightarrow{\mathrm{S}} e_{kl}(t)\, \delta(\mathbf{r}) \tag{A.26b}$$

I emphasize that the scaling limit applies to large clusters, where large means "of the order of the average cluster size $s(t)$." Thus Eq. (A.26b) shows that all correlations between large clusters are strictly *local* as $t \uparrow t_c$.

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REFERENCES

1. A. Suna, *Phys. Rev. B* **1**:1716 (1970).
2. N. G. van Kampen, *Int. J. Quant. Chem.: Quant. Chem. Symp.* **16**:101 (1982).
3. M. Doi, *J. Phys. A: Math. Gen.* **9**:1465, 1479 (1976).
4. P. Grassberger and M. Scheunert, *Fortschr. Phys.* **28**:547 (1980).
5. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
6. C. W. Gardiner, *Handbook of Stochastic Methods* (Springer-Verlag, Berlin, 1983).
7. G. Nicolis, F. Baras, and M. Malek Mansour, in *Non-equilibrium Dynamics in Chemical Systems*, C. Vidal and A. Pacault, eds. (Springer-Verlag, Berlin, 1984).
8. D. Elderfield, *J. Phys. A: Math. Gen.* **20**:L135 (1987).
9. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
10. W. H. Stockmayer, *J. Chem. Phys.* **11**:45 (1943).
11. R. M. Ziff, *J. Stat. Phys.* **23**:241 (1980).
12. M. von Smoluchowski, *Z. Phys. Chem.* **92**:129 (1917); *Phys. Z.* **17**:585 (1916).
13. R. L. Drake, in *Topics in Current Aerosol Research*, G. M. Hidy and J. R. Brock, eds. (Pergamon, New York, 1972), Part 2.
14. M. H. Ernst, in *Fractals in Physics*, L. Pietronero and E. Tosatti, eds. (North-Holland, Amsterdam, 1986).
15. W. T. Scott, *J. Atm. Sci.* **25**:54 (1967).
16. R. M. Ziff, M. H. Ernst, and E. M. Hendriks, *J. Phys. A: Math. Gen.* **16**:2293 (1983); *J. Colloid Interf. Sci.* **97**:266 (1984).
17. P. G. J. van Dongen and M. H. Ernst, *J. Stat. Phys.* **49**:927 (1987).
18. M. A. Burschka, Thesis, Utrecht (1985).
19. A. A. Lushnikov, *J. Colloid Interf. Sci.* **65**:276 (1978); *Izv. Akad. Nauk. SSSR Fiz. Atmos. Okeana* **14**:738 (1978).
20. Y. Kuramoto, *Prog. Theor. Phys.* **52**:711 (1974); see also *Prog. Theor. Phys.* **49**:1782 (1973).
21. P. G. J. van Dongen, *J. Stat. Phys.* **49**:927 (1987).
22. D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1985).
23. P. Meakin, T. Viscek, and F. Family, *Phys. Rev. B* **31**:564 (1985).
24. P. G. J. van Dongen, *J. Stat. Phys.* **53**:221 (1988).