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Spatial Fluctuations in Reaction-Diffusion Systems: A Model for Exponential Growth

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The spatial fluctuations in an exactly soluble model for the irreversible aggregation of clusters are treated. The model is characterized by *rate constants* $K_{ij} = i + j$ for the clustering of an i- and a j-mer, and *diffusion constants* $D_j = D$. It is assumed that $D \gg 1$ (reaction-limited aggregation). Explicit expressions for the correlation functions at equal and at different times are calculated. The equal-time correlation functions show scaling behavior in the scaling limit. The correlation length remains finite as $t \to \infty$, and the fluctuations become *large* at large times $(t \gg t_D)$ in *any* dimension. The crossover time t_D, at which the mean field theory (Smoluchowski's equation) breaks down, is given by $t_D \simeq \ln D$. These exact results imply that the upper critical dimension of this model is $d_c = \infty$ and, hence, that there is *no* unique upper critical dimension in models for the irreversible aggregation of clusters.

KEY WORDS: Spatial fluctuations; reaction-diffusion systems; aggregation; exponential growth; Smoluchowski theory.

1. INTRODUCTION

Within the field of nonequilibrium statistical mechanics, *irreversible growth processes* are a subject of continued interest. The interest is partly due to a multitude of fascinating physical phenomena (phase transitions, scale invariance, fractals), partly to the importance of technical applications. In many fields of science and technology one is therefore interested in mathematical predictions concerning the time evolution of aggregation processes. Pioneering work on the kinetic description of colloidal systems was done by von Smoluchowski.$^{(1)}$ Von Smoluchowski recognized that, in essence, cluster growth phenomena are complex *reaction-diffusion processes*, and

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can hence be described in terms of deterministic reaction-diffusion (or rate) equations.

In the rate equation approach to aggregation processes (Smoluchowski theory$^{(2,3)}$), spatial fluctuations are neglected. This is unfortunate for various reasons. First, from the point of view of stochastic theory, all the interesting information (such as production, spreading, and dissipation of correlations, or memory effects) is hidden in the fluctuations. Second, the size of the fluctuations provides a measure for the validity of the mean field theory: a description in terms of rate equations can be justified only if the fluctuations are *small.* Hence, it is of both theoretical and practical interest to study the spatial fluctuations about Smoluchowski's mean field approach. For this reason I present in this paper a model for the irreversible aggregation of clusters, where the spatial fluctuations can be studied in great detail.

To study the fluctuations I use a general method for describing fluctuations in reaction-diffusion systems, namely van Kampen's "method of compounding moments."$^{(4)}$ In ref. 5 this method was applied to an aggregation model containing a second-order phase transition (gelation). In ref. 6, I applied the method to a *second* (nongelling) model, which can be characterized by a moderately slow (linear) increase of the average cluster size as a function of time. The purpose of this paper is to study the spatial fluctuations in a *third model.* The model to be discussed in this paper differs notably from the models considered previously$^{(5,6)}$ in that: (i) the model is nongelling, and (ii) the aggregation process proceeds rather vehemently, and is characterized by a fast *(exponential)* increase of the average cluster size as a function of time.

Consider an aggregation process in a system of volume V, containing M monomeric units. Throughout, the unit of volume will be chosen such that the number density $M/V=1$, and I take the thermodynamic limit $(V\to\infty)$. In the aggregating system one has clusters of all possible sizes: monomers, dimers,.... In general a cluster containing k monomeric units is called a "k-mer," and the density of k-mers at position $\mathbf{r}$ and time t is denoted by $u_k(\mathbf{r}, t)$. The quantities of interest, to be studied below, are, first, the concentrations $\langle u_k(\mathbf{r}, t)\rangle = c_k(\mathbf{r}, t)$ and, second, the correlation functions $\langle \Delta u_m(\mathbf{r}_1, t_1)\, \Delta u_n(\mathbf{r}_2, t_2)\rangle$, where I define $\Delta u_m \equiv u_m - \langle u_m\rangle$. I distinguish between correlations at equal $(t_1=t_2)$ and at different times $(t_1<t_2)$. The basic assumption made in this paper is that the aggregation process is *reaction-limited,* i.e., that clusters diffuse over large distances (meet many other clusters) before they finally react. In this case it is possible$^{(4,5)}$ to derive closed kinetic equations for the average cluster numbers (concentrations) and the fluctuations about those averages.

The macroscopic law for the *concentrations* $c_k(\mathbf{r}, t)$ has in general the form of a complicated nonlinear reaction-diffusion equation. However, an important simplification occurs if the initial distribution is *spatially uniform*: $u_k(\mathbf{r}, 0) = c_k(0)$. This will be the case of main interest in this paper. If the initial state is spatially uniform, the concentrations are spatially uniform at all times: $c_k(\mathbf{r}, t) = c_k(t)$, and the macroscopic law takes the form

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

Here K_{ij} is the rate constant for the reaction between an i- and a j-mer. The rate equation (1.1) is known as Smoluchowski's coagulation equation$^{(1-3)}$ and has the property of mass conservation[2]: $\sum_k k c_k(t) = M/V = 1$.

Next consider the *spatial fluctuations* about the uniform non-equilibrium distribution $c_k(t)$. From the translational invariance of $u_k(\mathbf{r}, 0)$ it follows that the correlation functions depend only on the relative coordinates $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Instead of the equal-time correlation functions $\langle \Delta u_m\, \Delta u_n \rangle$ introduced above, it is convenient to consider the factorial cumulants $E_{mn}(\mathbf{r}, t)$, defined as

$$E_{mn}(\mathbf{r}, t) \equiv \langle \Delta u_m(\mathbf{r}_1, t)\, \Delta u_n(\mathbf{r}_2, t) \rangle - \delta_{mn} \delta(\mathbf{r})\, c_m(t) \tag{1.2}$$

The factorial cumulants E_{mn} satisfy a linear, inhomogeneous kinetic equation of the form

$$\frac{\partial}{\partial t} E_{mn}(\mathbf{r}, t) = \sum_{j=1}^{\infty} [A_{mj} E_{jn} + A_{nj} E_{mj}] + (D_m + D_n)\, \Delta E_{mn} - K_{mn} c_m c_n\, \delta(\mathbf{r}) \tag{1.3a}$$

where D_m is the diffusion constant for m-mers, and $\Delta = \partial^2/\partial \mathbf{r}^2$. The matrix A_{kj} in (1.3a) is defined as

$$A_{kj}(t) = -\sum_{i=1}^{\infty} K_{ij} c_i (\delta_{ik} + \delta_{jk} - \delta_{i+j,k}) \tag{1.3b}$$

and the initial condition is

$$E_{mn}(\mathbf{r}, 0) = -\delta(\mathbf{r})\, \delta_{mn} c_m(0) \tag{1.3c}$$

Equation (1.3) can be derived using the "method of compounding moments."$^{(4-6)}$ The physical meaning of the various terms in the right-hand

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[2] In this paper only *nongelling* systems are considered. Possible complications due to gel formation$^{(7)}$ need not worry us here.

side of (1.3a) is quite clear. The first term on the right couples the correlation functions E_{mn} linearly to the concentrations $c_k(t)$, and describes *dissipation* of fluctuations. The second term describes the spreading, or *diffusion*, of correlations, simply due to diffusion of m- and n-mers. Finally, the third terms on the right, proportional to $K_{mn}c_m c_n$, represents the *production* of new fluctuations due to reactions between m- and n-mers. The interplay of these three effects constitutes the physics of reaction-diffusion systems.

Next consider the two-time correlation functions $\kappa_{nm}(\mathbf{r}; t_2, t_1)$, defined as

$$\kappa_{nm}(\mathbf{r}; t_2, t_1) \equiv \langle \Delta u_m(\mathbf{r}_1, t_1)\, \Delta u_n(\mathbf{r}_2, t_2)\rangle \tag{1.4}$$

which satisfy a linearized version of the macroscopic law (1.1), namely

$$\frac{\partial}{\partial t}\kappa_{nm}(\mathbf{r}; t, t_1) = \sum_{j=1}^{\infty} A_{nj}\kappa_{jm} + D_n\,\Delta\kappa_{nm} \tag{1.5a}$$

to be solved with the initial condition

$$\kappa_{nm}(\mathbf{r}; t_1, t_1) = E_{mn}(\mathbf{r}, t_1) + \delta_{mn}\delta(\mathbf{r})\, c_m(t_1) \tag{1.5b}$$

The linearity of Eq. (1.5a) reflects the decay (dissipation and diffusion) of information about the state of the system at time t_1. The initial condition (1.5b) guarantees that κ_{nm} reduces to the correlation function $\langle \Delta u_m\, \Delta u_n\rangle$ at equal times ($t_2 = t_1$) in the limit $t_2 \downarrow t_1$.

In this paper I consider a *special model*, characterized by the reaction and diffusion constants

$$K_{ij} = i + j \qquad (i, j = 1, 2,...) \tag{1.6a}$$

$$D_m = D \qquad (m = 1, 2,...) \tag{1.6b}$$

The sum kernel (1.6a) is considered a realistic model in various fields of science. In polymer chemistry (1.6a) serves as a stylized version of the classical polymer model ARB_g of Flory and Stockmayer,(7–10) but it has also been used, e.g., in colloid science,(11,12) astrophysics,(13) cloud dynamics,(14,15) and aerosol research.(2,16) For $K_{ij} = i + j$, Smoluchowski's equation (1.1) can be solved exactly(15) for a general initial distribution $c_k(0)$. For example, for monodisperse initial conditions, $c_k(0) = \delta_{k1}$, one finds from (1.1) that $c_k(t)$ is given by

$$c_k(t) = (1-\tau)\frac{k^{k-1}}{\tau k!}(\tau e^{-\tau})^k; \qquad \tau \equiv 1 - e^{-t} \tag{1.7}$$

From (1.7) it follows that the average cluster size $s(t) \equiv \sum_k k^2 c_k(t)$ *increases exponentially*, $s(t) = e^{2t}$, while the concentrations $c_k(t)$ fall off algebraically at large times, $c_k(t) \sim (2\pi)^{-1/2} e^{-t} k^{-3/2}$ for $t \gg 1$. The model (1.6b) for the diffusion constants is the simplest possible choice,(17-19) and presumably the only one that leads to an exact solution for the correlation functions. Extensions to more general models are discussed in Section 6.

Concerning the fluctuations in the model $K_{ij} = i + j$, the following is known. The *nonspatial* fluctuations in finite systems were studied in refs. 11 and 20. Nonspatial fluctuations are fluctuations, purely due to reactions, in a "well-stirred" system, where the diffusion constant D is infinitely large. To my knowledge, the *spatial* fluctuations (for finite D) have not been studied before. However, there exists a simple relation between the spatial correlation functions $E_{mn}(\mathbf{r}, t)$ and $\kappa_{mn}(\mathbf{r}; t_2, t_1)$ and the nonspatial correlation functions $e_{mn}(t)$ and $\kappa_{nm}(t_2, t_1)$ calculated in ref. 20, namely

$$\int d\mathbf{r}\, E_{mn}(\mathbf{r}, t) = e_{mn}(t) \tag{1.8a}$$

$$\int d\mathbf{r}\, \kappa_{nm}(\mathbf{r}; t_2, t_1) = \kappa_{nm}(t_2, t_1) \tag{1.8b}$$

This shows that the nonspatial correlation functions ($D = \infty$) can also be interpreted as *global* correlation functions in the spatial problem (D finite).

Apart from theoretical considerations, there are also experimental results supporting the model $K_{ij} = i + j$ for the reaction constants. Some of the most interesting recent experiments on reaction-limited aggregation have been carried out by Weitz and collaborators,(21) who observe that (i) the average cluster size increases exponentially in time, while (ii) $c_k(t)$ falls off algebraically at large times, $c_k(t) \sim A(t) k^{-\tau}$, with an exponent $\tau \simeq 1.5$. As will be clear from (1.7), this is precisely what one would expect(22) if K_{ij} were given by (1.6a). Other experiments showing exponential growth are described in refs. 23 and 24. An exponent $\tau \simeq 3/2$ is found in ref. 25.

The plan of this paper is as follows. The equal-time correlations (1.2) are discussed in Section 2, and the two-time correlations (1.4) in Section 3. Section 4 investigates the influence of statistical fluctuations in the initial state: it is assumed that $u_k(\mathbf{r}, 0)$ is Poisson-correlated. In Section 5, I use the results obtained for the fluctuations to test the mean-field assumption underlying Smoluchowski's equation. The upper critical dimension for the model (1.6) is calculated in this section. Finally, Section 6 contains a discussion of the results. In the bulk of this paper I assume that the initial state of the system is monodisperse. However, Eq. (1.3) can be solved for general initial conditions. The solution is given in Appendix A. Appendix B is a technical appendix.

2. THE EQUAL-TIME CORRELATION FUNCTIONS

I consider only monodisperse initial conditions, $c_k(0)=\delta_{k1}$. In this case it is possible to obtain a relatively simple, explicit form for the equal-time correlation functions $E_{mn}(\mathbf{r}, t)$. In this section I sketch the method and give the results. Details are given in Appendices A and B.

The correlation functions $E_{mn}(\mathbf{r}, t)$ are determined by (1.3a), to be solved with the initial condition (1.3c). To solve Eq. (1.3), it is convenient to introduce the Fourier transform $F_{mn}(\mathbf{q}, t)$ of $E_{mn}(\mathbf{r}, t)$, i.e.,

$$F_{mn}(\mathbf{q}, t) \equiv \int d\mathbf{r}[\exp(i\mathbf{q}\cdot\mathbf{r})]\, E_{mn}(\mathbf{r}, t) \tag{2.1}$$

The kinetic equation for F_{mn} and its initial condition follow from (1.3) as

$$\begin{aligned} \frac{\partial}{\partial t} F_{mn}(\mathbf{q}, t) = \sum_{j=1}^{\infty} & [A_{mj}F_{jn} + A_{nj}F_{mj}] \\ & - K_{mn}c_m c_n - (D_m + D_n)q^2 F_{mn} \end{aligned} \tag{2.2a}$$

$$F_{mn}(\mathbf{q}, 0) = -\delta_{mn}c_m(0) \tag{2.2b}$$

Equation (2.2), with A_{kj} given by (1.3b), can be solved exactly for a *general* initial distribution $c_k(0)$ with the use of generating function techniques. The method and the results are presented in Appendix A. For monodisperse initial conditions the expression for the generating function found in Appendix A can in principle be inverted to yield the explicit form of $F_{mn}(\mathbf{q}, t)$ and $E_{mn}(\mathbf{r}, t)$. However, this calculation is rather lengthy, and it is much easier to simply verify that the outcome (to be presented below) satisfies Eq. (2.2). This check is carried out in Appendix B.

One finds the following results. The correlation functions $F_{mn}(\mathbf{q}, t)$ have a remarkably simple form as a function of the cluster sizes m and n, namely

$$F_{mn}(\mathbf{q}, t) = [\alpha_1(\mathbf{q}, t) + \alpha_2(\mathbf{q}, t)(m+n) + \alpha_3(\mathbf{q}, t)\, mn]\, c_m(t)\, c_n(t) \tag{2.3}$$

The concentrations $c_m(t)$ are given in (1.7). Note that the prefactor $[\cdots]$ in (2.3) has the same bilinear structure as was found previously$^{(6)}$ for the model $K_{ij}=1$. The $\mathbf{q}$ dependence of $F_{mn}(\mathbf{q}, t)$ is entirely contained in the functions $\alpha_i(\mathbf{q}, t)$ $(i=1, 2, 3)$, which have the relatively simple form

$$\alpha_i(\mathbf{q}, t) = \left[-e^{-2t}\delta_{i3} + \int_0^t dt'\, Q_i(t', t)(e^{2Dq^2t'} - 1) \right] e^{-2Dq^2t}, \qquad (i=1, 2, 3) \tag{2.4}$$

where $Q_i(t', t)$ is an integral kernel, to be specified below. From the form (2.2) it is already obvious that, for $\mathbf{q}=\mathbf{0}$, $F_{mn}(\mathbf{q}, t)$ reduces to the nonspatial cumulants $e_{mn}(t)$, discussed near (1.8):

$$F_{mn}(\mathbf{0}, t) = -e^{-2t} mn\, c_m(t)\, c_n(t) = e_{mn}(t) \tag{2.5}$$

In the second step of (2.5) I used the explicit form of $e_{mn}(t)$, known from ref. 20. For $E_{mn}(\mathbf{r}, t)$ it follows directly from (2.3) and (2.4) that

$$E_{mn}(\mathbf{r}, t) = [A_1(\mathbf{r}, t) + A_2(\mathbf{r}, t)(m+n) + A_3(\mathbf{r}, t)\, mn]\, c_m(t)\, c_n(t) \tag{2.6a}$$

where $A_i(\mathbf{r}, t)$ takes the form of a superposition of Gaussians,

$$A_i(\mathbf{r}, t) = \int_0^t dt'\, Q_i(t', t)[g(\mathbf{r}; 4D(t-t')) - g(\mathbf{r}; 4Dt)] - \delta_{i3}\, e^{-2t} g(\mathbf{r}; 4Dt) \tag{2.6b}$$

In (2.6b) I introduced the d-dimensional Gaussian distribution with zero mean and variance σ^2, denoted as $g(\mathbf{r}, \sigma^2)$.

The integral kernels $Q_i(t', t)$ in (2.4) are given for $i = 1, 2, 3$ by

$$Q_1(t', t) = -2(e^t - 1)^{-2} e^{2(t+t')}(t - t' + e^{-t} - 1)(t - t' - e^{-t'} + e^{-t}) \tag{2.7a}$$

$$\begin{aligned} Q_2(t', t) = {} & (e^t - 1)^{-2} e^{2t'}[2(t-t')^2 + 2(t-t')(e^{-t} - e^{-t'}) \\ & - (1 - e^{-t})(1 - e^{-t'})] \end{aligned} \tag{2.7b}$$

$$Q_3(t', t) = -2(e^t - 1)^{-2} e^{2(t'-t)}(t - t')(t - t' + 1 - e^{-t'}) \tag{2.7c}$$

The importance of the various terms in (2.3) or (2.6a) is different in different limits. Clearly, at all times, A_3 or Q_3 is dominant if one considers the limit of *large cluster sizes* ($m, n \to \infty$):

$$E_{mn}(\mathbf{r}, t) \sim A_3(\mathbf{r}, t)\, mnc_m(t)\, c_n(t) \qquad (m, n \to \infty) \tag{2.8}$$

On the other hand, at *large times* the first term on the right in (2.6a) is dominant. This may be seen from (2.6b) and (2.7). One finds that for $t \to \infty$

$$\begin{aligned} & A_1(\mathbf{r}, t) \sim e^{2t} \bar{A}_1(\mathbf{r}) \\ & \bar{A}_1(\mathbf{r}) \equiv -2 \int_0^\infty dt'\, e^{-2t'} t'(t' - 1)\, g(\mathbf{r}; 4Dt') \end{aligned} \tag{2.9a}$$

$$\begin{aligned} & A_2(\mathbf{r}, t) \sim \bar{A}_2(\mathbf{r}) \\ & \bar{A}_2(\mathbf{r}) \equiv \int_0^\infty dt'\, e^{-2t'}[2(t')^2 - 1]\, g(\mathbf{r}; 4Dt') \end{aligned} \tag{2.9b}$$

$$\begin{aligned} & A_3(\mathbf{r}, t) \sim e^{-2t} \bar{A}_3(\mathbf{r}) \\ & \bar{A}_3(\mathbf{r}) \equiv -2 \int_0^\infty dt'\, e^{-2t'} t'(t' + 1)\, g(\mathbf{r}; 4Dt') \end{aligned} \tag{2.9c}$$

For the large-time behavior of the correlation functions E_{mn} this implies

$$E_{mn}(\mathbf{r}, t) \sim e^{2t}\bar{A}_1(\mathbf{r})\, c_m(t)\, c_n(t) \qquad (t \to \infty) \tag{2.10}$$

Equation (2.10) gives rise to the important observation that the spatial profile of the fluctuations assumes a constant form as $t \to \infty$. The behavior of the correlations at large times is *not diffusive*: the correlation length remains finite!

The same phenomenon is observed in the *scaling limit* (S), which is the combined limit where the cluster sizes are large ($m, n \to \infty$), and the average cluster size $s(t)$ is large $[s(t) \to \infty]$, with the ratios $m/s(t)$ and $n/s(t)$ kept fixed. The average cluster size is defined as $s(t) \equiv \sum_k k^2 c_k(t)$. For the model $K_{ij} = i + j$, one finds from (1.1) that $s(t) = e^{2t}$. In the scaling limit it is known(26–28) that the concentrations $c_m(t)$ approach a simple scale-invariant form, described by a scaling function $\phi(u) \equiv (2\pi u^3)^{-1/2} e^{-u/2}$:

$$c_m(t) \xrightarrow{\mathrm{S}} s(t)^{-2} \phi(m/s(t)) \tag{2.11}$$

Similarly, using the results in (2.9), one finds that the spatial fluctuations, too, approach a scale-invariant form in the scaling limit:

$$F_{mn}(\mathbf{q}, t) \xrightarrow{\mathrm{S}} s(t)^{-3}\, \Phi(u_1, u_2, D^{1/2}\mathbf{q}) \tag{2.12a}$$

$$E_{mn}(\mathbf{r}, t) \xrightarrow{\mathrm{S}} s(t)^{-3}\, \eta(u_1, u_2, \mathbf{r}/D^{1/2}) \tag{2.12b}$$

where $u_1 \equiv m/s(t)$, $u_2 \equiv n/s(t)$. The scaling function η, which is simply related to Φ by Fourier transformation, is given by

$$\eta(u_1, u_2, \mathbf{r}/D^{1/2}) = [\bar{A}_1(\mathbf{r}) + \bar{A}_2(\mathbf{r})(u_1 + u_2) + \bar{A}_3(\mathbf{r}) u_1 u_2]\, \phi(u_1)\, \phi(u_2) \tag{2.13}$$

Note that in the scaling limit, too, the correlation length remains *finite*, of the order of $D^{1/2}$.

To what extent do the limiting results (2.8), (2.10), and (2.12) depend on the initial conditions? This question may be answered by applying the techniques developed in ref. 20 (Section 4) to the generating function of F_{mn} calculated in Appendix A. One finds that for general initial conditions: (i) the correlation function E_{mn}, with $m, n \to \infty$, has the same form as in (2.8), but the prefactor A depends on the initial distribution; (ii) at large times the basic feature of (2.10) is retained: $E_{mn}(\mathbf{r}, t)$ assumes a constant profile, but the profile depends on the initial conditions; (iii) the scaling law (2.12), (2.13) holds also for a general initial distribution: the scaling function η is universal, i.e., does not depend on $c_k(0)$.

Finally, having in hand the results (2.6) and (2.3) for $E_{mn}(\mathbf{r}, t)$ and $F_{mn}(\mathbf{q}, t)$, it is easy to calculate the density–density correlation function $\rho(\mathbf{r}, t)$ or its Fourier transform $\hat{\rho}(\mathbf{q}, t)$:

$$\hat{\rho}(\mathbf{q}, t) = \sum_{m,n} mn[F_{mn}(\mathbf{q}, t) + \delta_{mn} c_m(t)] \tag{2.14}$$

Insertion of (2.3) with (2.4) and (2.7) into (2.14) yields a very simple result

$$\hat{\rho}(\mathbf{q}, t) = (1 - e^{-2Dq^2 t}) + 2 \int_0^t dt' \, e^{2t'} [1 - e^{-2Dq^2(t-t')}] \tag{2.15}$$

in complete agreement with the general result, Eq. (6.6) of ref. 6. At large times one finds that

$$\hat{\rho}(\mathbf{q}, t) \sim e^{2t} \frac{Dq^2}{1 + Dq^2} \to \infty \qquad (t \to \infty;\ \text{all } \mathbf{q} \neq \mathbf{0}) \tag{2.16}$$

implying that, as $t \to \infty$, the density fluctuations grow exponentially fast at all length scales.

3. THE TWO-TIME CORRELATION FUNCTIONS

To calculate the correlation functions $\kappa_{nm}(\mathbf{r}; t_2, t_1)$ it is convenient to introduce the Fourier transform $\hat{\kappa}_{nm}(\mathbf{q}; t_2, t_1)$ of κ_{nm}. The Fourier transform satisfies a set of coupled ordinary differential equations,

$$\frac{\partial}{\partial t} \hat{\kappa}_{nm}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} A_{nj}(t)\, \hat{\kappa}_{jm}(\mathbf{q}; t, t_1) - Dq^2 \hat{\kappa}_{nm}(\mathbf{q}; t, t_1) \tag{3.1a}$$

to be solved with the initial condition

$$\hat{\kappa}_{nm}(\mathbf{q}; t_1, t_1) = F_{mn}(\mathbf{q}, t_1) + \delta_{mn} c_n(t_1) \tag{3.1b}$$

Equation (3.1) follows directly from Eq. (1.5) for κ_{nm}.

The kinetic equation (3.1) may be solved in various steps. The *first step* is to eliminate the last term on the right in (3.1a). For this purpose I introduce new functions a_{nm}, defined as

$$a_{nm}(\mathbf{q}; t, t_1) \equiv \hat{\kappa}_{nm}(\mathbf{q}; t, t_1)\, e^{Dq^2(t - t_1)} \tag{3.2}$$

The functions a_{nm} satisfy the simpler equation

$$\frac{\partial}{\partial t} a_{nm}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} A_{nj}(t)\, a_{jm}(\mathbf{q}; t, t_1) \tag{3.3}$$

and have the same initial value (3.1b) as $\hat{\kappa}_{nm}$. Note that (3.3) is a linear equation for a_{nm}. This implies that a_{nm} is completely determined by the evolution matrix $Y(t, t_1)$ connected with the matrix $A(t)$ in (3.3). The evolution matrix is defined by

$$\frac{\partial}{\partial t} Y_{nm}(t, t_1) = \sum_{j=1}^{\infty} A_{nj}(t)\, Y_{jm}(t, t_1) \tag{3.4a}$$

$$Y_{nm}(t_1, t_1) = \delta_{nm} \tag{3.4b}$$

Once Y in (3.4) is known, the solution a_{nm} of the problem (3.3) follows as

$$a_{nm}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} Y_{nj}(t, t_1)\, a_{jm}(\mathbf{q}; t_1, t_1) \tag{3.5}$$

with $a_{jm}(\mathbf{q}; t_1, t_1)$ given by (3.1b). To determine the evolution matrix Y will therefore be the *second step* in the calculation of $\hat{\kappa}_{nm}$.

The basic idea in the calculation of Y is that one can reduce the problem (3.4) to a problem that has already been solved in ref. 20. In this paper I calculated the evolution matrix $Y^0(t, t_1)$ belonging to a matrix $A^0(t)$, related to $A(t)$ in (1.3b) as

$$A^0_{nj}(t) = A_{nj}(t) + jc_n(t) \tag{3.6}$$

The evolution matrix Y^0 has the form[(20)]

$$Y^0_{nm}(t, t_1) = n\frac{\tau - \tau_1}{1 - \tau_1}\left[-c_n(t) + (1-\tau)\frac{(n\tau - m\tau_1)^{n-m-1}}{(n-m)!}\exp(m\tau_1 - n\tau)\right] \tag{3.7}$$

(where $\tau \equiv 1 - e^{-t}$ and $\tau_1 \equiv 1 - e^{-t_1}$) and has the properties

$$S_n(t, t_1) \equiv \sum_j Y^0_{nj}(t, t_1)\, jc_j(t_1) = e^{t_1 - t} nc_n(t) \tag{3.8a}$$

$$S^*_n(t, t_1) \equiv \sum_j Y^0_{nj}(t, t_1)\, c_j(t_1) = \frac{1}{\tau}\left[\tau_1 + (1-\tau)(\tau - \tau_1)n\right] c_n(t) \tag{3.8b}$$

As we shall see below, it is possible to express the evolution matrix Y in (3.4) in terms of Y^0.

To solve the problem (3.4), we substitute (3.6) into (3.4a):

$$\frac{\partial}{\partial t} Y_{nm}(t, t_1) = \sum_{j=1}^{\infty} A^0_{nj}(t)\, Y_{jm}(t, t_1) - c_n(t) \sum_{j=1}^{\infty} jY_{jm}(t, t_1) \tag{3.9}$$

Multiplying Eq. (3.4a), or (3.9), with n, and summing over all n yields $\sum_n nY_{nm} = \text{const}$. The initial condition (3.4b) implies that the constant is equal to m, so that (3.9) reduces to

$$\frac{\partial}{\partial t} Y_{nm}(t, t_1) = \sum_{j=1}^{\infty} A^0_{nj}(t)\, Y_{jm}(t, t_1) - mc_n(t) \tag{3.10}$$

The solution of (3.10) may easily be guessed from the form of the inhomogeneity in (3.10). One finds that

$$Y_{nm}(t, t_1) = Y^0_{nm}(t, t_1) + m\chi_n(t, t_1) \tag{3.11a}$$

where $\chi_n(t, t_1)$ has the form

$$\chi_n(t, t_1) \equiv [a(t, t_1) + b(t, t_1)n]\, c_n(t) \tag{3.11b}$$

and $a(t, t_1)$ and $b(t, t_1)$ are given by

$$a(t, t_1) = (e^{-t_1} - e^{-t} - t + t_1)/(1 - e^{-t}) \tag{3.12a}$$

$$b(t, t_1) = -e^{-t}[e^{-t_1} - e^{-t}(1 + t - t_1)]/(1 - e^{-t}) \tag{3.12b}$$

The result (3.11), (3.12) may be obtained by substituting (3.11) into (3.10) and using the explicit form of A^0_{nj} and c_n. One then obtains two differential equations for a and b that may readily be solved. The result is (3.12).

The third and final step is the calculation of $\hat{\kappa}_{nm}(\mathbf{q}; t_2, t_1)$. An explicit expression for $\hat{\kappa}_{nm}$ may be obtained by combining the relation (3.2) between $\hat{\kappa}_{nm}$ and a_{nm} with Eqs. (3.1b), (3.5), (3.8), and (3.11a). Inverse Fourier transformation of the result finally yields the two-time correlation functions $\kappa_{nm}(\mathbf{r}; t_2, t_1)$:

$$\begin{aligned} \kappa_{nm}(\mathbf{r}; t_2, t_1) = c_m(t_1)\{ & Y_{nm}(t_2, t_1)\, g(\mathbf{r}; 2D(t_2 - t_1)) \\ & + [A_1(\mathbf{r}; t_2, t_1) + A_2(\mathbf{r}; t_2, t_1)m][S^*_n(t_2, t_1) + \chi_n(t_2, t_1)] \\ & + [A_2(\mathbf{r}; t_2, t_1) + A_3(\mathbf{r}; t_2, t_1)m][S_n(t_2, t_1) + e^{2t_1}\chi_n(t_2, t_1)]\} \end{aligned} \tag{3.13}$$

Here S_n, S^*_n, and χ_n are defined, respectively, in (3.8a), (3.8b), and (3.11b) and

$$\begin{aligned} A_i(\mathbf{r}; t_2, t_1) \equiv & \int_0^{t_1} dt'\, Q_i(t', t_1)[g(\mathbf{r}; 2D(t_2 + t_1 - 2t')) - g(\mathbf{r}; 2D(t_2 + t_1))] \\ & - \delta_{i3} e^{-2t_1} g(\mathbf{r}; 2D(t_2 + t_1)) \end{aligned} \tag{3.14}$$

The d-dimensional Gaussian distribution $g(\mathbf{r}, \sigma^2)$ was introduced in (2.6b). Thus we find that κ_{nm} has a simple structure: basically it is a superposition of Gaussians.

To obtain some more insight into the wealth of information contained in κ_{nm}, we consider as an example the long-time behavior $(t_2 \to \infty)$ of the autocorrelation function $\kappa_{mm}(\mathbf{r}; t_2, t_1)$. At large times $(t_2 \to \infty)$ the terms in (3.13) proportional to S_n and S_n^* are negligible in comparison to χ_n, so that (3.13) simplifies to

$$\begin{aligned}\kappa_{mm}(\mathbf{r}; t_2, t_1) \sim c_m(t_1)\{ & Y^0_{mm}(t_2, t_1)\, g(\mathbf{r}; 2D(t_2 - t_1)) \\ & + \chi_m(t_2, t_1)[A_1 + mA_2 + e^{2t_1}(A_2 + mA_3) \\ & + mg(\mathbf{r}; 2D(t_2 - t_1))]\} \qquad (3.15)\end{aligned}$$

where $A_i \equiv A_i(\mathbf{r}; t_2, t_1)$. We further specialize to the case $\mathbf{r} = \mathbf{0}$, which corresponds to *local* memory effects in the system. Putting $\mathbf{r} = \mathbf{0}$ in (3.15), we find that $\kappa_{mm}(\mathbf{0}; t_2, t_1)$ behaves for $t_2 \to \infty$ as

$$\kappa_{mm}(\mathbf{0}; t_2, t_1) \sim \sigma(m, t_1)(4\pi D t_2)^{-d/2}\, c_m(t_1)\, c_m(t_2) \qquad (t_2 \to \infty) \qquad (3.16a)$$

where the prefactor $\sigma(m, t_1)$ is given by

$$\begin{aligned}\sigma(m, t_1) = {} & [-1 + m!\, e^{m\tau_1}/m^m(1 - \tau_1)]m \\ & - d\{q_1(t_1) + mq_2(t_1) + e^{2t_1}[q_2(t_1) + mq_3(t_1)] + mt_1\} \qquad (3.16b)\end{aligned}$$

and $q_i(t) \equiv \int_0^t dt'\, Q_i(t', t)\, t'$. Equation (3.16a) shows that the information about the number of m-mers at t_1 decays due to diffusion [factor $(Dt_2)^{-d/2}$] and due to reactions [factor $c_m(t_2)$], and finally there is a prefactor $\sigma(m, t_1)$ determining the sign of the correlations. Analysis of (3.16b) shows that $\sigma(m, t_1)$ is *positive* (as is to be expected) at sufficiently large times $[t_1 > T_0(m)]$ and *negative* at short times $[t_1 < T_0(m)]$, where the crossover time $T_0(m)$ is for large m given by $T_0(m) \sim \frac{1}{2} \ln m$. Thus we obtain the surprising result that a *deficiency* of m-mers somewhere in space at an early time t_1 implies on the average a *surplus* in the same region at large times.

4. POISSON INITIAL CONDITIONS

In the previous sections it was assumed that, initially, the system is strictly homogeneous: $u_k(\mathbf{r}, 0) = c_k(0)$ for all $\mathbf{r}$. In this section I investigate the influence of small deviations from the homogeneous initial state on the spatial fluctuations. In particular, it will be assumed that at $t = 0$ the clusters are distributed over the system according to Poisson statistics.(29)

First consider a large system (of volume $V \to \infty$ and mass $M = V$), whose initial state deviates slightly from the uniform state:

$$u_m(\mathbf{r}, 0) = c_m(0) + \xi_m(\mathbf{r}, 0) \tag{4.1}$$

The concentrations $c_m(0)$ are fixed by the requirement $\int_V d\mathbf{r}\, \xi_m(\mathbf{r}, 0) = 0$. I assume that the deviations $\xi_m(\mathbf{r}, 0)$ are *mesoscopic*, i.e., that the fluctuations $\int_v d\mathbf{r}\, \xi_m(\mathbf{r}, 0)$ in small cells ($v \ll V$, but $v \gg 1$) are at most of the order of $v^{1/2}$. In this case the average density $\langle u_m(\mathbf{r}, t)\rangle$, too, deviates mesoscopically from the uniform state:

$$\langle u_m(\mathbf{r}, t)\rangle \equiv c_m(t) + \langle \xi_m(\mathbf{r}, t)\rangle \tag{4.2}$$

where $c_m(t)$ is the solution of (1.1). The mesoscopic deviations from uniformity $\langle \xi_m(\mathbf{r}, t)\rangle$ satisfy the same linearized macroscopic law as the correlation functions κ_{nm}, i.e.,

$$\frac{\partial}{\partial t} \langle \xi_m(\mathbf{r}, t)\rangle = \sum_{j=1}^{\infty} A_{mj}(t) \langle \xi_j(\mathbf{r}, t)\rangle + D_m \Delta \langle \xi_m(\mathbf{r}, t)\rangle \tag{4.3}$$

to be solved subject to $\langle \xi_m(\mathbf{r}, 0)\rangle = \xi_m(\mathbf{r}, 0)$. Furthermore, it was shown in ref. 5 (Section 5) that the fluctuations about $\langle u_m(\mathbf{r}, t)\rangle$ are not affected by mesoscopic deviations in the initial state, i.e., that in this case the factorial cumulants are also given by $E_{mn}(\mathbf{r}, t)$ in (1.5).

Next consider an *ensemble* of systems (with volume V), all prepared in the same manner (macroscopically), but with small statistical fluctuations $\xi_m(\mathbf{r}, 0)$ in the initial state. I assume that, at $t = 0$, the m-mers ($m = 1, 2,\ldots$) are distributed according to Poisson statistics, i.e.,

$$\overline{\xi_m(\mathbf{r}, 0)} = 0 \tag{4.4a}$$

$$\overline{\xi_m(\mathbf{r}_1, 0)\, \xi_n(\mathbf{r}_2, 0)} = \delta(r_1 - r_2)\, \delta_{mn} c_m(0) \tag{4.4b}$$

The bar denotes an ensemble average. As a result of (4.4), the total mass M in the system is also a Poisson variable: $\bar{M} = V$ and $\overline{(M - V)^2} = V$. The *macroscopic law* in the ensemble follows directly from (4.2), (4.3), and (4.4a) as $\overline{\langle \xi_m(\mathbf{r}, t)\rangle} = 0$ or, equivalently, $\overline{\langle u_m(\mathbf{r}, t)\rangle} = c_m(t)$. The fluctuations about the ensemble average are described by the correlation function

$$E^*_{mn}(\mathbf{r}, t) \equiv \overline{\langle \xi_m(\mathbf{r}_1, t)\, \xi_n(\mathbf{r}_2, t)\rangle} - \delta_{mn} \delta(\mathbf{r})\, c_m(t) \tag{4.5}$$

where $\xi_m(\mathbf{r}, t) = u_m(\mathbf{r}, t) - c_m(t)$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Calculation of E^*_{mn} is the goal of this section.

The correlation function E^*_{mn} is in a simple way related to E_{mn} of Section 2, namely

$$E^*_{mn}(\mathbf{r}, t) = E_{mn}(\mathbf{r}, t) + \Pi_{mn}(\mathbf{r}, t) \tag{4.6}$$

where Π_{mn} is defined as

$$\Pi_{mn}(\mathbf{r}, t) \equiv \overline{\langle \xi_m(\mathbf{r}_1, t)\rangle \langle \xi_n(\mathbf{r}_2, t)\rangle} \tag{4.7}$$

The kinetic equation for Π_{mn} follows directly from (4.3) as

$$\frac{\partial}{\partial t} \Pi_{mn}(\mathbf{r}, t) = \sum_{j=1}^{\infty} [A_{mj} \Pi_{jn} + A_{nj} \Pi_{mj}] + (D_m + D_n) \Delta \Pi_{mn} \tag{4.8a}$$

$$\Pi_{mn}(\mathbf{r}, 0) = \delta_{mn} \delta(\mathbf{r})\, c_m(0) \tag{4.8b}$$

Equation (4.8b) follows directly from (4.4b). Combination of (4.8) and (1.3a) shows that E^*_{mn} is determined by the *same* equation (1.3a) as E_{mn}, but now with the initial condition $E^*_{mn}(\mathbf{r}, 0) = 0$. Therefore E^*_{mn} is given for general initial conditions by the results of Appendix A, and may be calculated by inversion of (A.12).

However, for monodisperse initial conditions it is much simpler to solve (4.8) directly. Its solution is easily seen to be

$$\Pi_{mn}(\mathbf{r}, t) = Y_{m1}(t, 0)\, Y_{n1}(t, 0)\, g(\mathbf{r}; 4Dt) \tag{4.9a}$$

where $Y_{m1}(t, 0)$ follows from (3.7) and (3.11) as

$$Y_{m1}(t, 0) = [a(t, 0) + m(b(t, 0) + e^{-t})]\, c_m(t) \tag{4.9b}$$

The correlation function E^*_{mn} then follows from combination of (4.9), (2.6), and (4.6).

Let us consider two special cases. First consider correlations for a *fixed value of* $\mathbf{r}$, with $t \to \infty$. In this case it follows from (2.10b) and (3.12) that the term Π_{mn} in (4.6) is (roughly) of relative order e^{-2t} and can be neglected. Thus we find that at large times, for a fixed value of $\mathbf{r}$, the memory of the initial state has faded away: the dominant fluctuations at large times are those generated during the reaction-diffusion process.

Next consider the *global* behavior of the fluctuations. The result in this case is completely different. From the definition (4.5) it is clear that $\int d\mathbf{r}\, E^*_{mn}$ gives the factorial cumulant of $N_m(t)$, the total number of m-mers in the system:

$$\int d\mathbf{r}\, E^*_{mn}(\mathbf{r}, t) = \frac{1}{V} [\overline{\langle (N_m - \overline{\langle N_m\rangle})(N_n - \overline{\langle N_n\rangle})\rangle} - \delta_{mn} \overline{\langle N_m\rangle}] \tag{4.10}$$

From (4.6) and (4.9a) one finds that

$$\int d\mathbf{r}\, E^*_{mn}(\mathbf{r}, t) = e_{mn}(t) + Y_{m1}(t, 0)\, Y_{n1}(t, 0)$$

$$= [a^2 + (m+n)(b+e^{-t})a + mn(2e^{-t}+b)b]\, c_m c_n \quad (4.11)$$

with $a = a(t, 0)$ and $b = b(t, 0)$ given by (3.12). Obviously $\int d\mathbf{r}\, E^*_{mn}$ vanishes at $t = 0$: we started from a Poisson distribution. For $t > 0$ we see from (3.12) that $a(t, 0)$ and $b(t, 0)$ are negative, so that

$$\int d\mathbf{r}\, E^*_{mn}(\mathbf{r}, t) \sim -\tfrac{1}{2}t(m+n+2mn)\, c_m c_n < 0 \qquad (t \downarrow 0) \qquad (4.12a)$$

$$\int d\mathbf{r}\, E^*_{mn}(\mathbf{r}, t) \sim t^2 c_m c_n > 0 \qquad (t \to \infty) \qquad (4.12b)$$

Consequently, the numbers $N_m(t)$ $(m = 1, 2,...)$ follow *sub*-Poisson statistics if t is sufficiently small $[t < T_1(m, n)]$, and *super*-Poisson statistics if t is large $[t > T_1(m, n)]$. The crossover time T_1 is, e.g., given for $m = n \gg 1$ by $T_1(m, m) \sim \ln m$. Note that the large-time behavior in (4.12b) is entirely determined by $\Pi_{mn}(\mathbf{r}, t)$, i.e., by the memory of the initial state.

5. UPPER CRITICAL DIMENSION IN THE MODEL $K_{ij} = i + j$

The upper critical dimension d_c is the boundary dimension for the validity of the mean field approximation (Smoluchowski's equation) at *large* times. For dimensions $d > d_c$ the fluctuations about the mean field solutions are small, and the mean field theory predicts the correct asymptotic behavior as $t \to \infty$. For $d < d_c$ the fluctuations are large, and the predictions from the rate equation are incorrect at large times.(18,30,31) Note that the definition of d_c emphatically refers to the *large-time limit*: at short and intermediate times the rate equation is always applicable due to the assumption $D \gg 1$ (reaction-limited aggregation).

In ref. 5, Section 4.5, a criterion was developed for the validity of the mean-field approach (Smoluchowski's equation) at long times $(t \to \infty)$. The criterion simply states that the reaction part of the rate equation for the number of k-mers in a cell of size v contains a macroscopic contribution $S_k(t)$ and a contribution due to fluctuations $F_k(t)$,

$$\frac{\partial}{\partial t}\int_v d\mathbf{r}\, \langle u_k(\mathbf{r}, t)\rangle_R = S_k(t) + F_k(t) \qquad (5.1a)$$

and that the mean-field description is applicable as long as the fluctuations are *small*:

$$R_k(t) = |F_k(t)/S_k(t)| \ll 1 \tag{5.1b}$$

The contributions $S_k(t)$ and $F_k(t)$ are given by integrals over a cell of volume v. Their explicit form is

$$S_k(t) = v\dot{c}_k(t) \tag{5.2a}$$

$$F_k(t) = \frac{1}{2} \sum_{i+j=k} K_{ij} \int_v d\mathbf{r}\, E_{ij}(\mathbf{r}, t) - \sum_{j=1}^{\infty} K_{kj} \int_v d\mathbf{r}\, E_{kj}(\mathbf{r}, t) \tag{5.2b}$$

with $\dot{c}_k$ given by (1.1)

The cell size v occurs in (5.2) since, in order to derive the kinetic equations (1.1) and (1.3), one has to *discretize* the space.[4,29] The cell size v is *bounded from below* by the requirement (5.1b) that the fluctuations are small. An *upper bound* on v follows from the requirement that the cell diameter should be small compared to: (i) the correlation length, in order that the discretization of the diffusion terms is allowed; and (ii) the distance traveled by a cluster during its lifetime, in order that the mean field assumption within each cell is allowed. Physically it is rather obvious that condition (ii) *implies* condition (i). From Section 2 we know that the correlation length at large times is $D^{1/2}$, so that the cell size is in any case bounded from above by $v \ll D^{d/2}$. The mean field theory breaks down as soon as the upper and the lower bounds on the cell size can no longer be reconciled.

The behavior of $S_k(t)$ and $F_k(t)$ at large times follows from (1.7), (2.6), and (2.9) as

$$\left.\begin{aligned} S_k(t) &\sim -vc_k(t) \qquad &(5.3\text{a})\\ F_k(t) &\sim -\int_v d\mathbf{r}\, [A_1(\mathbf{r}, t) + M_2(t)\, A_2(\mathbf{r}, t)]\, c_k(t) \qquad &(5.3\text{b}) \end{aligned}\right\} \quad (t \to \infty)$$

so that the criterion (5.1) yields, with the use of (2.9),

$$R_k(t) \sim v^{-1} e^{2t} \left| \int_0^\infty dt'\, e^{-2t'}(2t' - 1) \int_v d\mathbf{r}\, g(\mathbf{r}; 4Dt') \right| \ll 1 \tag{5.4}$$

Analysis of (5.4) shows that the large-time behavior of $R_k(t)$ is different in different dimensions:

$$\begin{aligned} R_k(t) &\propto e^{2t} D^{-1/2} \qquad &(d = 1,\ t \to \infty) \qquad &(5.5\text{a})\\ &\propto e^{2t} D^{-1} \ln(D/v) \qquad &(d = 2,\ t \to \infty) \qquad &(5.5\text{b})\\ &\propto e^{2t} D^{-1} v^{-(d-2)/d} \qquad &(d > 2,\ t \to \infty) \qquad &(5.5\text{c}) \end{aligned}$$

but in all cases $R_k(t)$ increases exponentially with time. The proportionality constants in (5.5) depend only on the dimension d.

The large-time behavior (5.5) of $R_k(t)$ gives rise to two remarks. First, the upper critical dimension d_c is the dimension above which the fluctuations remain finite (and small) as $t \to \infty$. From (5.5) we see that such a dimension does not exist, i.e., that the upper critical dimension for the model $K_{ij} = i + j$ is $d_c = \infty$. Note that $d = 2$ is a special dimension (bringing additional logarithms), at least as far as the *prefactor* of e^{2t} is concerned. However, these differences in prefactor (and hence the speciality of $d = 2$) are utterly irrelevant at large times. At the moment the general feeling,(32–35) mainly based on the model $K_{ij} = 1$ (see Section 6), seems to be that the upper critical dimension in aggregation processes is $d_c = 2$. The exactly soluble model $K_{ij} = i + j$ shows that this is not so: the value of d_c is model dependent.

The second remark is that one can use (5.5) to obtain an estimate of the region of validity of the mean field approach. From (5.1) it follows that the mean field approach breaks down if $R_k(t) \simeq 1$, which happens at large times ($t > t_D$). An estimate for the time t_D at which the Smoluchowski approach breaks down may be determined from (5.5). To obtain an upper bound on t_D, we drop the logarithm in (5.5b) and set $v = D^{d/2}$ in (5.5c). The result is $t_D \simeq (d/4) \ln D$ for all $d \geqslant 1$.

What are the implications of the upper bound $t_D \simeq (d/4) \ln D$ for aggregation experiments? To see this, consider $d = 3$ and focus on a monodisperse initial distribution. Let the volume fraction of the suspension be ρ. In the units of this paper, the typical lifetime T of a monomer is of the order of unity, $T \simeq 1$. If the sticking probability in a collision is p and the average collision time is τ_b, then clearly $T = \tau_b/p$. On the other hand, τ_b is equal to von Smoluchowski's(1) "coagulation time" (he considered $p = 1$), so that $\tau_b \simeq (4\pi D R v_0)^{-1}$. Here R is the radius of a monomer (in our units $R \simeq \rho^{1/3}$), and v_0 is the number density (in our units $v_0 = 1$). Hence one finds that $D \simeq (4\pi p)^{-1} \rho^{-1/3}$, which yields the *estimate*

$$t_D \simeq \tfrac{3}{4} \ln(4\pi p \rho^{1/3})^{-1} \tag{5.6}$$

In polymerization experiments, where, for instance,(8) $\rho \simeq 10^{-3}$ and $p = 10^{-9}$–10^{-13}, this would imply $t_D \simeq 15$–20.

6. EXTENSIONS AND DISCUSSION

I start the discussion with an extension to more general models of the *scaling behavior* of the fluctuations found in Section 2. For this purpose it is convenient to consider the large class of *homogeneous kernels*(27,28) characterized by exponents μ, ν, and λ, i.e.,

$$K(i, j) = a^{-\lambda} K(ai, aj) \qquad (\text{all } a > 0) \tag{6.1a}$$

$$K(i, j) \sim i^{\mu} j^{\nu} \qquad (j \gg i;\ \mu + \nu = \lambda) \tag{6.1b}$$

For such kernels it is known(27,28) that $\lambda > 1$ corresponds to gelling and $\lambda \leqslant 1$ to nongelling models. Only nongelling models ($\lambda \leqslant 1$) are considered in this paper. Concerning the diffusion coefficients, it is assumed that D_k falls off algebraically, $D_k \sim Dk^{-\alpha}$, with an exponent $\alpha \geqslant 0$.

Scaling laws for homogeneous kernels are readily obtained. In the presentation I distinguish kernels (like $K_{ij} = i + j$) with $\lambda = 1$, and kernels (like $K_{ij} = 1$) with $\lambda < 1$.

Consider models with $\lambda = 1$ first.[3] For the special model $K_{ij} = i + j$ it was found in Section 2 that the fluctuations show scaling behavior, independent of the initial conditions. The scaling law is given by Eq. (2.12a) or (2.12b). Could it be that this scaling law holds generally for homogeneous kernels? To investigate this question, we substitute the scaling form (2.12a) into the kinetic equation (2.2a) and check whether (2.12a) is consistent. Using the results of ref. 20, Section 7.2, one finds the following results. If the diffusion constants are *independent* of the cluster size ($\alpha = 0$), then (2.12) is indeed consistent for all homogeneous kernels with $\lambda = 1$ and $\mu = 0$. If, on the other hand, $\alpha > 0$, one finds that $F_{mn}(\mathbf{q}, t)$ satisfies the *same* scaling law (2.12a), but with $D^{1/2}\mathbf{q}$ replaced by $[Ds(t)^{-\alpha}]^{1/2}\mathbf{q}$. Similarly one finds for the correlation functions E_{mn} in position space that

$$E_{mn}(\mathbf{r}, t)\, d\mathbf{r} \xrightarrow{\mathrm{S}} s(t)^{-3} \eta(u_1, u_2, \mathbf{R})\, d\mathbf{R} \tag{6.2a}$$

where $u_1 = m/s(t)$, $u_2 = n/s(t)$, and

$$\mathbf{R} \equiv \mathbf{r}/r_1(t); \qquad r_1(t) \equiv [Ds(t)^{-\alpha}]^{1/2} \tag{6.2b}$$

The scaling limit S is defined such that $\mathbf{R}$ is kept fixed as $s(t) \to \infty$. Note that the general scaling law (6.2) reduces to the previous result (2.12b) if $\alpha = 0$.

The length $r_1(t)$ in the scaling law (6.2) plays the role of a *correlation length.* In the exactly soluble model $K_{ij} = i + j$, with $D_k = D$, the correlation length remains finite as $t \to \infty$, namely $r_1(t) \to D^{1/2}$, so that the correlations are *localized* at large times. The general result (6.2) shows that the

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[3] I consider only kernels (like $K_{ij} = i + j$) with $\lambda = 1$ and $\mu = 0$. Kernels with $\lambda = 1$ and $\mu > 0$ are special,(28) and have, to my knowledge, never been proposed as realistic models for irreversible aggregation.

correlations are always localized for $\lambda = 1$: the correlation length $r_1(t)$ approaches a constant if $\alpha = 0$, and *decreases* as a function of time if $\alpha > 0$. This decrease is due to the immobility of large clusters $[k \simeq s(t)]$.

Next consider models with a degree of homogeneity $\lambda < 1$. For such models it was shown in ref. 6 that the fluctuations show scaling behavior of a slightly different form, namely

$$E_{mn}(\mathbf{r}, t)\, d\mathbf{r} \xrightarrow{S'} s(t)^{-3}\, \eta(u_1, u_2, \mathbf{R}')\, d\mathbf{R}' \tag{6.3a}$$

$$\mathbf{R}' \equiv \mathbf{r}/r_0(t); \qquad r_0(t) \equiv [Dts(t)^{-\alpha}]^{1/2} \tag{6.3b}$$

The definition of the limit S′ in (6.3) differs from that of S in (6.2) in that $\mathbf{R}'$ (instead of $\mathbf{R}$) is kept fixed as $s(t) \to \infty$. The scaling law (6.3) in the limit S′ is valid also for models with $\lambda = 1$, but in this case the result is somewhat trivial.(6) One finds for $\lambda = 1$ that the profile of the fluctuations contracts to a delta peak: $\eta(u_1, u_2, \mathbf{R}') = \eta(u_1, u_2)\, \delta(\mathbf{R}')$. This only shows that the relevant length scale $r_1(t)$ for $\lambda = 1$ is *smaller* than the relevant length $r_0(t)$ in (6.3).

In the exactly soluble model $K_{ij} = 1$, with $D_k = D$, the correlation length increases in the same manner as for pure diffusion: $r_0(t) = (Dt)^{1/2}$. From the generalization (6.3) for $\lambda < 1$, in combination with the known(27,28) time dependence of the average cluster size, $s(t) = s_0 t^{1/(1-\lambda)}$, it follows that $r_0(t) \propto (Dt^{\beta})^{1/2}$ as $t \to \infty$, with an exponent $\beta \equiv (1 - \alpha - \lambda)/(1 - \lambda)$. This shows that the sum of the exponents $\alpha + \lambda$ determines the time evolution of the correlation length: $r_0(t)$ *increases* with time if $\alpha + \lambda < 1$, approaches a constant if $\alpha + \lambda = 1$, and *decreases* if $\alpha + \lambda > 1$. Note that purely diffusive behavior $(\beta = 1)$ is obtained only for $\alpha = 0$. For $\alpha > 0$ one finds $\beta < 1$, so that in this case $r_0(t)$ grows more slowly than in pure diffusion. Localization occurs if $\alpha + \lambda \geqslant 1$.

The second subject to be discussed is the value of the upper critical dimension, $d_c = \infty$, found in Section 5. Concerning upper critical dimensions in aggregation processes, the following is known. For the simple model A + B → inert, with $c_A(0) = c_B(0)$, or

$$K_{ij} = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1} \tag{6.4}$$

it was shown by Toussaint and Wilczek(36) and Kang and Redner(30) that $d_c = 4$. Kang and Redner also showed that $d_c = 2$ for the model A + A → inert, or $K_{ij} = \delta_{i1}\delta_{j1}$, and conjectured $d_c = 2$ for A + A → A. This conjecture was proved by Peliti.(37) The relevance of A + A → A for aggregation processes is that $K_{ij} = 1$, with $D_k = D$, implies this reaction if one considers only the *number* of clusters.(30) Finally, Elderfield(34) argued in perturbation theory that $d_c = 2$ for the *reversible* reactions $\mathrm{A} + \mathrm{A} \rightleftarrows \mathrm{A}$

and $A_i + A_j \rightleftarrows A_{i+j}$ (with $K_{ij} = 1$ and $D_k = D$). This result, in combination with computer simulations,$^{(17-19,38,39)}$ has led to the feeling$^{(32-35)}$ that generally $d_c = 2$ in aggregation processes, in spite of the exactly soluble counterexample (6.4).

In this paper I showed that $d_c = \infty$ for $K_{ij} = i + j$ with $D_k = D$. Could this result also be obtained from perturbation theory?$^{(34,37)}$ To see this, consider a field theory where the evolution operator can be represented as a path integral with action $S = S_0 + S_1$. The free part S_0 of the action describes the diffusion, the perturbation S_1 describes the reactions. The propagator corresponding to S_0 is purely diffusive, and so are the zeroth-order correlation functions $E^{(0)}_{mn}(\mathbf{r}, t)$. Now consider the nonperturbative large-time results (2.10), or the scaling law (2.12), which show that the correlation length remains *finite*, $r_1(t) \sim D^{1/2}$, as $t \to \infty$. It seems that this result can never be obtained from finite-order perturbation theory about a *diffusive* free theory. Thus, it seems essential to use the real, instead of the free propagators. The situation here is reminiscent of epidemics with sensibilization, where Cardy$^{(40)}$ has shown that the free fixed point is unstable in any dimension.

The time dependence of the correlation lengths $r_1(t)$ and $r_0(t)$ discussed above shows that the correlation functions are *nondiffusive* for all homogeneous kernels with $\lambda = 1$, and for kernels with $\lambda < 1$ provided that $\alpha > 0$. For such models there is no basis for an upper critical dimension $d_c = 2$. Indeed, one can show that generally $d_c = \infty$ for models with localized correlations ($\alpha + \lambda \geqslant 1$). For models with $\alpha + \lambda < 1$ it is possible to show that the upper critical dimension is given by $d_c = 2/(1 - \alpha - \lambda)$. Details concerning these results can be found in Ref. 41.

What does our result for $\lambda = 1$ imply for experiments? I emphasize that $d_c = \infty$ does *not* imply that Smoluchowski's equation is invalid. The mean field approach is perfectly suited, provided that the aggregation process is reaction limited and the times considered are not too large. Deviations are to be expected only at large times. Meakin$^{(32)}$ suggests, on the basis of computer simulations, that the experiments of Weitz *et al.*$^{(21)}$ and von Schulthess *et al.*$^{(25)}$ have not yet reached their asymptotic stage. This paper supplies analytic evidence that this suggestion is presumably correct: at large times one expects the reaction to slow down in comparison to the Smoluchowski theory due to spatial fluctuations. Recently some very interesting DLA and RLA experiments were published by Broide.$^{(33)}$ Broide finds that his results can reasonably well be decribed by $K_{ij} \simeq i + j$ at short, but not at large times. At time $t \simeq 10$ there occurs a crossover from exponential growth to moderately slow behavior. Actually, on the basis of our estimate (5.6) and Broide's experimental data ($d = 3$, $\rho \simeq 2.5 \times 10^{-5}$, $p \simeq 1/500$) one would expect a crossover already at an earlier time ($t_D \simeq 6$).

My expectation is that the observed crossover at $t \simeq 10$ is a direct consequence of large spatial fluctuations.

Finally, I summarize the results. The subject of this paper was a model for irreversible aggregation, characterized by exponential growth of the mean cluster size. The equal-time and two-time correlation functions have been calculated exactly for a spatially uniform and monodisperse initial distribution. The *equal-time correlation functions* approach a scale-invariant form (independent of the initial conditions) in the scaling limit. Moreover, at large times the correlation length approaches a finite constant, $r_1 \sim D^{1/2}$, and the density fluctuations diverge at all length scales. The *two-time correlation functions* contain a wealth of information. For example, the m-mer autocorrelation function shows that a deficiency at an early time implies a surplus in the same region at large times. Our results for the *Poisson initial condition* (Section 4) show that the correlation functions are not very sensitive to statistical fluctuations in the initial state: the memory of the initial state fades away rather quickly, provided one considers correlations at finite distances. The *upper critical dimension* in this model is $d_c = \infty$. The mean field approximation (Smoluchowski's equation) breaks down in any finite dimension at a time $t_D \simeq (d/4) \ln D$. In $d = 3$ this implies $t_D \simeq (3/4) \ln(4\pi p \rho^{1/3})^{-1}$, where p is the sticking probability and ρ the volume fraction.

APPENDIX A

This Appendix gives the exact solution of Eq. (2.2) for the factorial cumulants $F_{mn}(\mathbf{q}, t)$. The solution is valid for a general initial distribution $c_k(0)$ and is formulated in terms of the generating function of F_{mn}.

To solve Eq. (2.2), we need some results for the solution $c_k(t)$ of the macroscopic law (1.1) with $K_{ij} = i + j$. Equation (1.1) may be solved in terms of the generating function $F(x, t)$ of $c_k(t)$, i.e.,

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

which satisfies a nonlinear partial differential equation

$$\frac{\partial F}{\partial t} = F\left(\frac{\partial F}{\partial x} - 1\right) \tag{A.2}$$

The solution $F(x, t)$ of Eq. (A.2) is implicitly given by

$$F(x, t) = e^{-t} u(z); \qquad z(x, t) \equiv F(x, t) - x \tag{A.3a}$$

The function $u(z)$ is determined by the initial condition $F(x, 0) \equiv v(x)$. We also need an expression for the x derivative of F:

$$\frac{\partial F}{\partial x}(x, t) = u'(z)/[u'(z) - e^t] \tag{A.3b}$$

The moments $M_n(t) \equiv \sum_k k^n c_k(t)$ $(n = 0, 1, 2)$ are given for general initial conditions by $M_0(t) = M_0(0)e^{-t}$, $M_1(t) = 1$, and $M_2(t) = M_2(0)e^{2t}$. More details concerning $c_k(t)$ or $F(x, t)$ can be found in ref. 15 or in Appendix A of ref. 20.

Equation (2.2) can now be solved for general initial conditions by introducing the generating function $H(x, y; \mathbf{q}, t)$ of $F_{mn}(\mathbf{q}, t)$, defined as

$$H(x, y; \mathbf{q}, t) \equiv \sum_{m,n} F_{mn}(\mathbf{q}, t)(e^{mx} - 1)(e^{ny} - 1) \tag{A.4}$$

If the generating function H is known, F_{mn} can be calculated by inversion of (A.4):

$$F_{mn}(\mathbf{q}, t) = \left(\frac{1}{2\pi i}\right)^2 \oint \frac{dw_1}{w_1^{m+1}} \oint \frac{dw_2}{w_2^{n+1}} H(x, y; \mathbf{q}, t) \tag{A.5}$$

where $w_1 \equiv e^x$ and $w_2 \equiv e^y$. The integration paths in (A.5) circle the origin in the complex w_1 and w_2 plane once in the counterclockwise direction.

To obtain an equation for H in (A.4), we multiply (2.2) with $(e^{mx} - 1)(e^{ny} - 1)$ and sum over all m and n. This yields a linear inhomogeneous partial differential equation for H,

$$\begin{aligned} \frac{\partial H}{\partial t} = {} & \left[\frac{\partial F}{\partial x}(x, t) + \frac{\partial F}{\partial y}(y, t) - 2 - 2Dq^2\right] H \\ & + F(x, t)\left[\frac{\partial H}{\partial x} - \frac{\partial H}{\partial x}(0, y; \mathbf{q}, t)\right] \\ & + F(y, t)\left[\frac{\partial H}{\partial y} - \frac{\partial H}{\partial y}(x, 0; \mathbf{q}, t)\right] \\ & - F(y, t)\left[\frac{\partial F}{\partial x}(x, t) - 1\right] - F(x, t)\left[\frac{\partial F}{\partial y}(y, t) - 1\right] \end{aligned} \tag{A.6a}$$

to be solved with the initial condition

$$H(x, y; \mathbf{q}, 0) = v(x) + v(y) - v(x + y) \tag{A.6b}$$

In (A.6b) we used the initial condition (2.2b) for $F_{mn}(\mathbf{q}, t)$ and the definition $v(x) \equiv F(x, 0)$. The difficulty in (A.6) is that (A.6a) is not a closed equation for $H(x, y; \mathbf{q}, t)$: it also contains derivatives $(\partial H/\partial x)(0, y)$ and $(\partial H/\partial y)(x, 0)$, which have to be calculated separately. Since the subsequent calculations are rather straightforward, we only sketch the derivation and simply give the results.

An equation for the derivative $(\partial H/\partial x)(0, y)$ may be obtained by differentiating Eq. (A.6a) with respect to x, and setting $x=0$ in the result. Unfortunately, this equation, too, is not closed: it contains the second derivative $(\partial^2 H/\partial x\,\partial y)(0, 0)$. For convenience we define

$$\frac{\partial H}{\partial x}(0, y; \mathbf{q}, t) \equiv H_x(y; \mathbf{q}, t) \tag{A.7a}$$

$$\frac{\partial^2 H}{\partial x\,\partial y}(0, 0; \mathbf{q}, t) \equiv H_{xy}(\mathbf{q}, t) \tag{A.7b}$$

Fortunately, the equation for $H_{xy}(\mathbf{q}, t)$ is *closed*, as may be seen by differentiation of the equation for H_x. The solution is easily found as

$$H_{xy}(\mathbf{q}, t) = \left[H_{xy}(\mathbf{q}, 0) - 2\int_0^t dt'\, M_2(t') e^{2Dq^2t'} \right] e^{-2Dq^2t} \tag{A.8a}$$

$$= -M_2(0)\left[1 + 2\int_0^t dt'\, e^{2(1+Dq^2t')} \right] e^{-2Dq^2t} \tag{A.8b}$$

In (A.8b) I used the initial condition (2.2b) for $F_{mn}(\mathbf{q}, 0)$ and the explicit form of the second moment $M_2(t)$.

The differential equation for $H_x(y; \mathbf{q}, t)$ simplifies drastically if we transform from the original variables (y, t) to new variables (z_2, t), where $z_2 \equiv z(y, t)$ is defined in (A.3a). The function H_x in terms of the new variables is denoted by H_x', i.e.,

$$H_x(y; \mathbf{q}, t) \equiv H_x'(z_2; \mathbf{q}, t) \tag{A.9}$$

The new function H_x' satisfies a simple *ordinary* differential equation in the t variable, which may readily be solved:

$$H_x'(z_2; \mathbf{q}, t) = [u'(z_2) - e^t]^{-1} e^{-2Dq^2t} \times \{[u'(z_2) - 1]\, H_x'(z_2; \mathbf{q}, 0) + I(z_2; \mathbf{q}, t)\} \tag{A.10a}$$

$$= [u'(z_2) - e^t]^{-1} e^{-2Dq^2t}[-1 + I(z_2; \mathbf{q}, t)] \tag{A.10b}$$

In (A.10b) I used the initial condition $F_{mn}(\mathbf{q}, 0)$ in (2.2b). The function $I(z; \mathbf{q}, t)$ is defined as

$$I(z; \mathbf{q}, t) = -\int_0^t dt'\, e^{2Dq^2t'}\{e^{t'} + e^{-t'}u(z) \times [u'(z) - e^{t'}][H_{xy}(\mathbf{q}, t') + M_2(t')]\} \tag{A.10c}$$

The function $H_x(y; \mathbf{q}, t)$ then follows from (A.9).

The final step is the calculation of $H(x, y; \mathbf{q}, t)$ in (A.6). We use the same trick as in (A.9), and transform from the old variables (x, y, t) to new variables (z_1, z_2, t), with $z_1 \equiv z(x, t)$ and $z_2 \equiv z(y, t)$:

$$H(x, y; \mathbf{q}, t) \equiv H'(z_1, z_2; \mathbf{q}, t) \tag{A.11}$$

As the result one finds an ordinary differential equation for H'. Its solution is

$$H'(z_1, z_2; \mathbf{q}, t) = e^{-2Dq^2t}\left[\frac{u'(z_1) - 1}{u'(z_1) - e^t}\frac{u'(z_2) - 1}{u'(z_2) - e^t} H'(z_1, z_2; \mathbf{q}, 0) + R(z_1, z_2; \mathbf{q}, t) + R(z_2, z_1; \mathbf{q}, t)\right] \tag{A.12a}$$

where $R(z_1, z_2; \mathbf{q}, t)$ is defined as

$$R(z_1, z_2; \mathbf{q}, t) \equiv -u(z_1)\int_0^t dt'\, e^{(2Dq^2-1)t'}\frac{u'(z_1) - e^{t'}}{u'(z_1) - e^t}\frac{u'(z_2) - e^{t'}}{u'(z_2) - e^t} \times \left[H'_x(z_2; \mathbf{q}, t) + \frac{e^{t'}}{u'(z_2) - e^{t'}}\right] \tag{A.12b}$$

The initial value $H'(z_1, z_2; \mathbf{q}, 0)$ in (A.12b) may be obtained from (A.6b) and (A.3) as

$$H'(z_1, z_2; \mathbf{q}, 0) = v(x_0) + v(y_0) - v(x_0 + y_0) \tag{A.13a}$$

where x_0 and y_0 are related to z_1 and z_2 by

$$x_0 \equiv u(z_1) - z_1; \qquad y_0 \equiv u(z_2) - z_2 \tag{A.13b}$$

Equations (A.12) and (A.13) determine the generating function H of F_{mn} in terms of the initial distribution $c_k(0)$, or $u(z)$.

I add several remarks. First, for monodisperse initial conditions, $c_k(0) = \delta_{k1}$, the result (A.12) for the generating function may be inverted to yield the explicit results (2.3)–(2.7) for $F_{mn}(\mathbf{q}, t)$. However, these calculations are so lengthy that I prefer the presentation of Appendix B. Second, one can use the result (A.12) to obtain the asymptotic behavior of $F_{mn}(\mathbf{q}, t)$ in various limits. These results are given at the end of Section 2. Third, the result (A.12) is valid also for the Poisson initial conditions of Section 4. In this case one has $F^*_{mn}(\mathbf{q}, t) = 0$ instead of (2.2b). The generating function H^* of F^*_{mn} is obtained by putting $H_{xy}(\mathbf{q}, 0) = 0$ in (A.8a), $H'_x(z_2; \mathbf{q}, 0) = 0$ in (A.10a), and $H'(z_1, z_2; \mathbf{q}, 0) = 0$ in (A.12a).

APPENDIX B

In this Appendix it is verified that the explicit expressions (2.3), (2.4), and (2.7) for $F_{mn}(\mathbf{q}, t)$ represent indeed the solution of Eq. (2.2) if $c_k(0) = \delta_{k1}$. The calculation consists of two steps. In the first step I show that F_{mn} has the form (2.3), and derive a set of coupled differential equations for the functions $\alpha_i(\mathbf{q}, t)$ $(i = 1, 2, 3)$. In the second step it is shown that this set of equations is solved by $\alpha_i(\mathbf{q}, t)$ in (2.4) and (2.7).

To obtain a more explicit form of Eq. (2.2), insert A_{kj} in (1.3b) into (2.2). For the model $K_{ij} = i + j$, one finds that

$$\begin{aligned} \frac{\partial}{\partial t} F_{mn}(\mathbf{q}, t) = &- [2 + (m+n) M_0(t) + 2Dq^2] F_{mn} - (m+n) c_m c_n \\ &- m c_m \sum_j F_{jn} - c_m \sum_j j F_{jn} + \sum_{i+j=m} m c_i F_{jn} \\ &- n c_n \sum_j F_{mj} - c_n \sum_j j F_{mj} + \sum_{i+j=n} n c_i F_{mj} \end{aligned} \tag{B.1}$$

Next we substitute the form (2.3) for F_{mn} into (B.1). The *left*-hand side contains the concentrations c_m and c_n and their time derivatives $\dot{c}_m$ and $\dot{c}_n$. The same is true for the *right*-hand side if we use

$$\sum_j F_{jn} = [(\alpha_1 + \alpha_2 n) M_0 + (\alpha_2 + \alpha_3 n)] c_n \tag{B.2a}$$

$$\sum_j j F_{jn} = [(\alpha_1 + \alpha_2 n) + (\alpha_2 + \alpha_3 n) M_2] c_n \tag{B.2b}$$

$$\sum_{i+j=m} m c_i F_{jn} = [2(\alpha_1 + \alpha_2 n) + m(\alpha_2 + \alpha_3 n)][\dot{c}_m + c_m(1 + m M_0)] c_n \tag{B.2c}$$

In (B.2c) I used Smoluchowski's equation (1.1).

Next insert (B.2) into (B.1) and collect the terms proportional to $c_m c_n$, $\dot{c}_m c_n$, and $c_m \dot{c}_n$. The result is

$$\begin{aligned}
\dot{c}_m c_n(\alpha_1+\alpha_2 n) + c_m \dot{c}_n(\alpha_1+\alpha_2 m) &= c_m c_n[(\dot{\alpha}_1 + 2Dq^2\alpha_1 + 2\alpha_2 M_2) \\
&\quad + (m+n)(\dot{\alpha}_2 + 1 + 2Dq^2\alpha_2 + \alpha_3 M_2 + \alpha_2) \\
&\quad + mn(\dot{\alpha}_3 + 2Dq^2\alpha_3 + 2\alpha_3)]
\end{aligned} \tag{B.3}$$

Dividing Eq. (B.3) by $c_m c_n$, using Eq. (1.7), i.e.,

$$\dot{c}_m/c_m = (1/\tau)[m(1-\tau)^2 - 1] \tag{B.4}$$

and comparing prefactors of 1, $m+n$, and mn yields

$$\dot{\alpha}_1 = -\left(\frac{2}{\tau} + 2Dq^2\right)\alpha_1 - 2M_2\alpha_2 \tag{B.5a}$$

$$\dot{\alpha}_2 = \frac{1}{\tau}e^{-2t}\alpha_1 - \left(1 + \frac{1}{\tau} + 2Dq^2\right)\alpha_2 - M_2\alpha_3 - 1 \tag{B.5b}$$

$$\dot{\alpha}_3 = \frac{2}{\tau}e^{-2t}\alpha_2 - 2(1+2Dq^2)\alpha_3 \tag{B.5c}$$

Here $\tau = 1 - e^{-t}$, as usual. The initial condition for (B.5) is

$$\alpha_1(\mathbf{q}, 0) = \alpha_2(\mathbf{q}, 0) = 0; \qquad \alpha_3(\mathbf{q}, 0) = -1 \tag{B.6}$$

This follows from the requirement $E_{mn}/e_{mn} \to \delta(\mathbf{r})$, or $F_{mn}/e_{mn} \to 1$ as $t \downarrow 0$. Note that the system (B.5) has the linear form $\dot{\boldsymbol{\alpha}} = A\boldsymbol{\alpha} + \boldsymbol{\alpha}_0$, with a matrix $A(t)$ that has a singularity at $t = 0$.

The second step in the calculation is to verify that (2.4) and (2.7) solve the set of equations (B.5) for $\alpha_i(\mathbf{q}, t)$. Transformation from α_i to new functions χ_i, defined by

$$\chi_i(\mathbf{q}, t) \equiv e^{2Dq^2t}\alpha_i(\mathbf{q}, t) \qquad (i = 1, 2) \tag{B.7a}$$

$$\chi_3(\mathbf{q}, t) \equiv e^{2(1+Dq^2)t}\alpha_3(\mathbf{q}, t) + 1 \tag{B.7b}$$

yields the following set of equations for $\chi_i(\mathbf{q}, t)$:

$$\dot{\chi}_1 = -\frac{2}{\tau}\chi_1 - 2e^{2t}\chi_2 \tag{B.8a}$$

$$\dot{\chi}_2 = \frac{1}{\tau}e^{-2t}\chi_1 - \left(1 + \frac{1}{\tau}\right)\chi_2 - \chi_3 - (e^{2Dq^2t} - 1) \tag{B.8b}$$

$$\dot{\chi}_3 = \frac{2}{\tau}\chi_2 \tag{B.8c}$$

to be solved with $\chi_i(\mathbf{q}, 0) = 0$. According to (2.4), χ_i has the form

$$\chi_i(\mathbf{q}, t) = \int_0^t dt'\, \Gamma_i(t', t)(e^{2Dq^2t'} - 1) \tag{B.9a}$$

with

$$\Gamma_1 = Q_1; \qquad \Gamma_2 = Q_2; \qquad \Gamma_3 = e^{2t}Q_3 \tag{B.9b}$$

Substitution of (B.9a) into (B.8) shows that (B.9) solves (B.8) provided that

$$\frac{\partial}{\partial t}\Gamma_1 = -\frac{2}{\tau}\Gamma_1 - 2e^{2t}\Gamma_2 \tag{B.10a}$$

$$\frac{\partial}{\partial t}\Gamma_2 = \frac{1}{\tau}e^{-2t}\Gamma_1 - \left(1 + \frac{1}{\tau}\right)\Gamma_2 - \Gamma_3 \tag{B.10b}$$

$$\frac{\partial}{\partial t}\Gamma_3 = \frac{2}{\tau}\Gamma_2 \tag{B.10c}$$

where Γ_i is short for $\Gamma_i(t', t)$. It is now an elementary calculation to show that Γ_i in (B.9b), with Q_i given by (2.7), is indeed the solution of (B.10).

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