Journal of Statistical Physics, Vol. 53, Nos. 1/2, 1988

Fluctuations in Reaction-Diffusion Systems: A New Exactly Soluble Growth Model

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Received March 25, 1988

The "method of compounding moments" devised by Van Kampen is used to study the spatial fluctuations in a model describing the irreversible formation of clusters. The reaction and diffusion constants in this model are chosen *independent* of the cluster sizes. For a monodisperse initial distribution explicit expressions are calculated for the equal-time and two-time correlation functions of the concentrations of m- and n-mers. For general initial conditions the fluctuations in the mass density are considered and a scaling theory is presented for the fluctuations at large times. Extensions to more general models are discussed.

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

1. INTRODUCTION

A very attractive method for studying reaction-diffusion systems is Van Kampen's "method of compounding moments."(1) Its value lies in its transparancy and its straightforwardness. In reaction-diffusion processes the aim is to derive kinetic equations for the concentrations of the reactants and for their correlation functions. According to the "method of compounding moments," this derivation proceeds in two steps. First one discretizes the space, and one constructs a master equation for a cell model: the particles may jump from cell to cell, and react within each cell. The kinetic equations for the averages and correlation functions are then derived *directly from the master equation for the cell model.* The second step is to transform back from the cell picture to a continuum formulation, replacing the cell index in the kinetic equations by the spatial coordinates **r** and the occupation numbers by particle densities.

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In a previous paper$^{(2)}$ I used the "method of compounding moments" to study the spatial fluctuations in a model describing the irreversible aggregation of clusters. Here I present a *new aggregation model*, for which the kinetic equations derived in ref. 2 can be solved exactly. In these aggregation models, I distinguish clusters of all possible sizes: monomers, dimers, and, in general, "k-mers." The clusters are involved in two processes: they diffuse and they react with other clusters. I make one basic assumption, namely that clusters travel over large distances (meet many other clusters) before they finally react. Thus, I restrict consideration to aggregation processes that are reaction limited.

What are the quantities of interest in these aggregating systems? Let us denote the density of k-mers by $u_k(\mathbf{r}, t)$. First one has the average density (*concentration*) of k-mers, $c_k(\mathbf{r}, t) \equiv \langle u_k(\mathbf{r}, t) \rangle$. A second quantity of interest is the *correlation function* $\langle \Delta u_m(\mathbf{r}_1, t_1)\, \Delta u_n(\mathbf{r}_2, t_2) \rangle$ which relates the fluctuation $\Delta u_m \equiv u_m - \langle u_m \rangle$ at position $\mathbf{r}_1$ and time t_1 to the fluctuation Δu_n at $\mathbf{r}_2$ and t_2. Throughout I adopt the convention that $t_2 \geqslant t_1 \geqslant 0$. With the use of the method of compounding moments, one can derive kinetic equations for the concentrations and the correlation functions. These derivations have been given in ref. 2; here I quote only the results.[2]

Before I address the fluctuations, I consider first the *macroscopic law* for the concentrations $c_k(\mathbf{r}, t)$. For *general* initial distributions $c_k(\mathbf{r}, 0)$, the concentrations satisfy an infinite set of coupled nonlinear reaction-diffusion equations that is far too complicated to be solved exactly. This is unfortunate, since we are interested in the fluctuations about $c_k(\mathbf{r}, t)$, and the fluctuations can be calculated only *after* the macroscopic law has been solved. However, there is one important special case where the problem becomes relatively simple, namely if the initial distribution is *spatially uniform*: $c_k(\mathbf{r}, 0) = c_k(0)$. In this case the solution $c_k(\mathbf{r}, t)$ of the reaction-diffusion problem is also spatially uniform: $c_k(\mathbf{r}, t) = c_k(t)$, where $c_k(t)$ satisfies Smoluchowski's coagulation equation$^{(3-5)}$

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

Here K_{ij} is the rate constant for the reaction between i- and j-mers. Note that the diffusion constants D_k do not enter in the macroscopic law (1.1). Equation (1.1) has the property of mass conservation: $\sum_{k=1}^{\infty} k c_k(t) = \text{const.}$ Throughout this paper I set this constant (which represents the mass

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[2] Actually, in ref. 2 I considered a model describing a phase transition (gelation) that required a special treatment. In this paper I do *not* consider the post-gel stage of gelling models, so that one can set the gel density equal to zero in the results of ref. 2, Section 2. This yields the results to be quoted below [Eqs. (1.1)–(1.5)].

density) equal to unity. Moreover, I take the thermodynamic limit, and consider the case of an *infinite* volume.

Next consider the correlation functions, where one distinguishes correlations at equal and at different times (corresponding to $t_2 = t_1$ and $t_2 > t_1$, respectively). The present choice of a uniform initial distribution implies that the correlation functions depend only on the relative coordinates $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, or (more precisely) on the modulus $|\mathbf{r}|$. The correlations at *equal* times can most conveniently be expressed in terms of the so-called factorial cumulants $E_{mn}(\mathbf{r}, t)$,(1) or, rather, in their Fourier transform $F_{mn}(\mathbf{q}, t)$:

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

$$F_{mn}(\mathbf{q}, t) \equiv \int d\mathbf{r}\, [\exp(i\mathbf{q}\cdot\mathbf{r})]\, E_{mn}(\mathbf{r}, t) \tag{1.2b}$$

The equal-time correlation functions can be determined from (1.2) once F_{mn} is known. The kinetic equation for F_{mn} is

$$\frac{\partial}{\partial t} F_{mn}(\mathbf{q}, t) = \sum_{j=1}^{\infty} (A_{mj}F_{jn} + A_{nj}F_{mj}) - K_{mn}c_m c_n - (D_m + D_n)\, q^2 F_{mn} \tag{1.3a}$$

where D_k is the diffusion constant of a k-mer and A_{kj} is defined as

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

Equation (1.3) is to be solved with the initial condition $F_{mn}(\mathbf{q}, 0) = -\delta_{mn}c_m(0)$. An important special case of (1.3) is obtained for $\mathbf{q} = \mathbf{0}$. In this case $F_{mn}(\mathbf{q}, t)$ reduces to the nonspatial factorial cumulants $e_{mn}(t)$ studied in refs. 6 and 7. From (1.2) it follows that $F_{mn}(\mathbf{0}, t)$ has the interpretation of an integrated correlation function: it shows how the fluctuation $\Delta u_m(\mathbf{r}, t)$ is correlated with the fluctuation in the total number of n-mers in the system.

The *two-time* correlation functions also depend only on $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and hence can be denoted as

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

Again it is more convenient to consider the Fourier transform $\hat{\kappa}_{nm}$ of κ_{nm}, which satisfies a set of coupled ordinary differential equations

$$\frac{\partial}{\partial t} \hat{\kappa}_{nm}(\mathbf{q}; t, t_1) = \sum_{j=1}^{\infty} A_{nj}\hat{\kappa}_{jm}(\mathbf{q}; t, t_1) - D_n q^2 \hat{\kappa}_{nm}(\mathbf{q}; t, t_1) \tag{1.5a}$$

to be solved with the initial condition

$$\hat{\kappa}_{nm}(\mathbf{q}; t_1, t_1) = F_{mn}(\mathbf{q}, t_1) + \delta_{mn} c_n(t_1) \tag{1.5b}$$

The condition (1.5b) simply states that the correlation functions for $t_2 > t_1$ should reduce to those for $t_2 = t_1$ in the limit $t_2 \downarrow t_1$.

In this paper we consider one particular model, corresponding to reaction and diffusion constants *independent* of the cluster sizes:

$$K_{ij} = 1; \qquad D_k = D \qquad (i, j, k = 1, 2, \ldots) \tag{1.6}$$

The macroscopic law for this model, i.e., Eq. (1.1) with $K_{ij} = 1$, has a long history. The properties of the solution $c_k(t)$ were studied by Smoluchowski$^{(3)}$ and subsequently by many authors, including van Kampen (see the acknowledgment in ref. 8). The fluctuations in this model were studied in ref. 7 for the spatially homogeneous ("well-stirred") case. The *spatial* fluctuations in the model $K_{ij} = 1$ have not been studied before.

The plan of this paper is as follows. Sections 2–4 are devoted to the equal-time correlations. In Section 2 I solve Eq. (1.3) for a *general* (but spatially uniform) initial distribution $c_k(0)$. The solution is formulated in terms of the generating function of F_{mn}. An explicit expression for F_{mn} (and E_{mn}) is given in Section 3 for *monodisperse* initial conditions, $c_k(0) = \delta_{k1}$. A novel scaling behavior of F_{mn} and E_{mn}, independent of the initial conditions, is found in Section 4. Section 5 is devoted to the two-time correlation functions. In Section 6 I discuss the behavior of the density fluctuations. This section is generally valid, provided that $D_k = D$: the conclusions hold for general initial conditions and general reaction rates K_{ij}. Further extensions are discussed in Section 7.

2. EXACT SOLUTION OF EQ. (1.3) FOR GENERAL INITIAL CONDITIONS

The kinetic equation (1.3) for the Fourier-transformed factorial cumulants $F_{mn}(\mathbf{q}, t)$ can be solved with the use of generating function techniques. From the structure of Eq. (1.3) it is clear that $F_{mn}(\mathbf{q}, t)$ can be calculated only after the macroscopic law has been solved. For this reason I recall some of the properties of $c_k(t)$ first.

The macroscopic law (1.1), with rate constants $K_{ij} = 1$, can be solved in terms of the generating function of the concentrations $c_k(t)$,

$$F(x, t) \equiv \sum_{k=1}^{\infty} c_k(t)(e^{kx} - 1) \tag{2.1}$$

The generating function $F(x, t)$ satisfies a simple ordinary differential equation $\partial F/\partial t = F^2/2$, which has the solution

$$F(x, t) = v(x)/[1 - \tfrac{1}{2}tv(x)] \tag{2.2}$$

if $v(x) \equiv F(x, 0)$. More details concerning $c_k(t)$ can be found in refs. 3 and 9 or in appendix A of ref. 7.

To solve the kinetic equation (1.3) for $F_{mn}(\mathbf{q}, t)$ with $K_{ij} = 1$ we introduce the generating function

$$H(x, y; \mathbf{q}, t) \equiv \sum_{m,n} F_{mn}(\mathbf{q}, t)(e^{mx} - 1)(e^{ny} - 1) \tag{2.3}$$

which satisfies the differential equation

$$\frac{\partial H}{\partial t} = [F(x, t) + F(y, t) - 2Dq^2] H - F(x, t)\, F(y, t) \tag{2.4a}$$

The initial condition for Eq. (2.4) follows from the initial value $F_{mn}(\mathbf{q}, 0) = -\delta_{mn} c_m(0)$ of F_{mn} as

$$H(x, y; \mathbf{q}, 0) = v(x) + v(y) - v(x + y) \tag{2.4b}$$

For fixed values of x, y, and $\mathbf{q}$, Eq. (2.4a) is an ordinary differential equation with respect to t, and may readily be integrated with the use of (2.2). The result is

$$H(x, y; \mathbf{q}, t) = \{[1 - \tfrac{1}{2}tv(x)][1 - \tfrac{1}{2}tv(y)]\}^{-2}\, e^{-2Dq^2t} V(x, y; \mathbf{q}, t) \tag{2.5a}$$

where I introduced

$$\begin{aligned} &V(x, y; \mathbf{q}, t) \\ &\quad \equiv H(x, y; \mathbf{q}, 0) - v(x)\, v(y) \int_0^t d\tau \\ &\quad\quad \times \{1 - \tfrac{1}{2}\tau[v(x) + v(y)] + \tfrac{1}{4}\tau^2 v(x)\, v(y)\}\, e^{2Dq^2\tau} \end{aligned} \tag{2.5b}$$

and $H(x, y; \mathbf{q}, 0)$ is given by (2.4b). Equation (2.5) represents an *exact* expression for F_{mn}, or E_{mn}, in terms of its generating function.

3. EXPLICIT FORM OF E_{mn} FOR MONODISPERSE INITIAL CONDITIONS

The special case of monodisperse initial conditions (monomers only at $t = 0$) corresponds to $c_k(0) = \delta_{k1}$ or $v(x) = F(x, 0) = e^x - 1$, so that in this case Eq. (2.4b) can also be written as $H(x, y; \mathbf{q}, 0) = -v(x)\,v(y)$. As a consequence, Eq. (2.5) assumes the form

$$\begin{aligned} H(x, y; \mathbf{q}, t) &\\ = -&\frac{v(x)\,v(y)}{[1-\frac{1}{2}tv(x)]^2\,[1-\frac{1}{2}tv(y)]^2} \\ &\times \{\beta_1(\mathbf{q}, t) + \beta_2(\mathbf{q}, t)[v(x)+v(y)] + \beta_3(\mathbf{q}, t)\,v(x)\,v(y)\} \qquad (3.1\text{a}) \end{aligned}$$

where the coefficients $\beta_i(\mathbf{q}, t)$ $(i = 1, 2, 3)$ are defined as

$$\begin{aligned} \beta_i(\mathbf{q}, t) &= \delta_{i1} \exp(-2Dq^2 t) \\ &\quad + \int_0^t d\tau\, (-\tfrac{1}{2}\tau)^{i-1} \exp[-2Dq^2(t-\tau)], \qquad i = 1, 2, 3 \qquad (3.1\text{b}) \end{aligned}$$

The results (3.1) for the generating function H can readily be inverted to yield an explicit expression for $F_{mn}(\mathbf{q}, t)$. One finds that

$$F_{mn}(\mathbf{q}, t) = [\alpha_1(\mathbf{q}, t) + \alpha_2(\mathbf{q}, t)(m+n) + \alpha_3(\mathbf{q}, t)\,mn]\,c_m(t)\,c_n(t) \qquad (3.2\text{a})$$

where the coefficients $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ are linearly related to the coefficients $\boldsymbol{\beta} = (\beta_1, \beta_2, \beta_3)$ in (3.1), namely

$$\boldsymbol{\alpha}(\mathbf{q}, t) = A(t) \cdot \boldsymbol{\beta}(\mathbf{q}, t) \qquad (3.2\text{b})$$

where the matrix $A(t)$ is given by

$$A(t) = -[t(2+t)]^{-2} \begin{pmatrix} t^4 & 8t^2(1+t) & 16(1+t)^2 \\ -2t^3 & -4t(2+3t) & -16(1+t) \\ 4t^2 & 16t & 16 \end{pmatrix} \qquad (3.2\text{c})$$

The simplest way to see that (3.2) is indeed the inverse of (3.1) is to start from (3.2) and calculate its generating function (2.3). One then finds (3.1a) as the result.

The factorial cumulants $E_{mn}(\mathbf{r}, t)$ can be obtained by inverse Fourier transformation of F_{mn} in (3.2). It follows immediately from (3.2a) that $E_{mn}(\mathbf{r}, t)$ has the form

$$E_{mn}(\mathbf{r}, t) = [A_1(\mathbf{r}, t) + A_2(\mathbf{r}, t)(m+n) + A_3(\mathbf{r}, t)\,mn]\,c_m(t)\,c_n(t) \qquad (3.3)$$

where $\mathbf{A}(\mathbf{r}, t) = A(t) \cdot \mathbf{B}(\mathbf{r}, t)$, and $\mathbf{B}(\mathbf{r}, t)$ is the inverse Fourier transform of $\boldsymbol{\beta}(\mathbf{q}, t)$ in (3.1b):

$$B_i(\mathbf{r}, t) = \delta_{i1}\, g(\mathbf{r}; 4Dt) + \int_0^t d\tau\, (-\tfrac{1}{2}\tau)^{i-1}\, g(\mathbf{r}; 4D(t-\tau)) \qquad (3.4)$$

Here I introduced the d-dimensional Gaussian distribution,

$$g(\mathbf{r};\sigma^2) \equiv (2\pi\sigma^2)^{-d/2} \exp(-\mathbf{r}^2/2\sigma^2) \tag{3.5}$$

The equal-time correlation functions follow immediately from (1.2a).

4. NOVEL SCALING BEHAVIOR OF THE SPATIAL FLUCTUATIONS

Consider again *general* initial conditions and focus on the *scaling limit* (S). The scaling limit is the limit where the average cluster size diverges $[s(t) \to \infty]$ and the cluster size $m \to \infty$, with the ratio $z \equiv m/s(t)$ fixed. As the definition of average cluster size I choose $s(t) \equiv \sum_{k=1}^{\infty} k^2 c_k(t)$. Different definitions are possible but lead to qualitatively the same results.[10] The average cluster size becomes large at large times; in our case one finds that $s(t) \sim t$ as $t \to \infty$.

In the scaling limit one finds that the concentrations $c_k(t)$ approach a simple scale-invariant form, independent of the initial conditions (see, e.g., Appendix A of ref. 7):

$$c_k(t) \xrightarrow{\text{S}} s(t)^{-2}\, \phi(k/s(t)) \tag{4.1}$$

where the scaling function $\phi(z)$ is given by $\phi(z) = 4e^{-2z}$. Clearly, if $c_k(t)$ shows scaling behavior, then so does its generating function $F(x, t)$ in (2.1). The appropriate definition of the "scaling limit" of a generating function follows from (2.1) as $s(t) \to \infty$ and $x \to 0$, with the product $\rho \equiv -xs(t)$ fixed. A question that presents itself is: would E_{mn} and F_{mn} and the generating function H also show simple scaling behavior, independent of the initial conditions?

This question can be investigated along the lines of ref. 7 (Section 4.3), and one finds that the answer is positive. For instance, consider the generating function H in (2.5). The scaling behavior of H can be expressed in terms of the *three* scaling variables $\rho_1 \equiv -xs(t)$, $\rho_2 \equiv -ys(t)$, and $\theta \equiv 2Dq^2t$. One finds that

$$H(x, y; \mathbf{q}, t) \xrightarrow{\text{S}} s(t)^{-1}\, \Psi(\rho_1, \rho_2, \theta) \tag{4.2a}$$

where the scaling function Ψ is given by

$$\Psi(\rho_1, \rho_2, \theta) = -\frac{16\rho_1\rho_2}{(2+\rho_1)^2\,(2+\rho_2)^2} \times \int_0^1 du\, [1 + \tfrac{1}{2}(\rho_1+\rho_2)u + \tfrac{1}{4}\rho_1\rho_2 u^2]\, e^{-\theta(1-u)} \tag{4.2b}$$

The result (4.2) is valid both if $\mathbf{q}$ and if θ is kept fixed when taking the scaling limit. Physically, however, the latter case is more interesting, since q values of the order of $(Dt)^{-1/2}$ correspond to distances of the order of $(Dt)^{1/2}$. Thus, the generating function H approaches a simple scaling form in the product space $(x, y, \mathbf{q})$. Note that (4.2) is *independent* of the initial conditions.

The result (4.2) can now be inverted to yield a scaling form for $F_{mn}(\mathbf{q}, t)$. The simplest way to obtain the result is to employ the fact that (4.2) is independent of the initial conditions and take the scaling limit in (3.2), which was derived for monodisperse initial conditions. As the result, one finds that F_{mn} approaches a relatively simple scaling form,

$$F_{mn}(\mathbf{q}, t) \xrightarrow{S} s(t)^{-3}\, \Phi(z_1, z_2, \theta) \tag{4.3a}$$

where $z_1 \equiv m/s(t)$, $z_2 \equiv n/s(t)$, and

$$\Phi(z_1, z_2, \theta) = [a_1(\theta) + a_2(\theta)(z_1 + z_2) + a_3(\theta)\, z_1 z_2]\, \phi(z_1)\, \phi(z_2) \tag{4.3b}$$

The coefficients $\mathbf{a} = (a_1, a_2, a_3)$ are given by $\mathbf{a}(\theta) = L \cdot \mathbf{b}(\theta)$, where the matrix L and the vector $\mathbf{b}$ are defined as

$$L = -\begin{pmatrix} 1 & 2 & 1 \\ -2 & -3 & -1 \\ 4 & 4 & 1 \end{pmatrix}; \qquad b_i(\theta) = \int_0^1 du\, (-2u)^{i-1}\, e^{-\theta(1-u)}, \qquad i = 1, 2, 3 \tag{4.4}$$

The scaling law (4.3) is valid for general initial conditions and could, if desired, be derived directly from (4.2).

A scaling form for E_{mn} can be obtained by Fourier inversion of (4.3). In terms of the scaling variable $\mathbf{R} \equiv \mathbf{r}/(4Dt)^{1/2}$ one finds that

$$E_{mn}(\mathbf{r}, t)\, d\mathbf{r} \xrightarrow{S} s(t)^{-3}\, \eta(z_1, z_2, \mathbf{R})\, d\mathbf{R} \tag{4.5a}$$

where the scaling function η is given by

$$\eta(z_1, z_2, \mathbf{R}) = [A_1(\mathbf{R}) + A_2(\mathbf{R})(z_1 + z_2) + A_3(\mathbf{R})\, z_1 z_2]\, \phi(z_1)\, \phi(z_2) \tag{4.5b}$$

with $\mathbf{A}(\mathbf{R}) = L \cdot \mathbf{B}(\mathbf{R})$ and

$$B_i(\mathbf{R}) = \int_0^1 du\, (2\pi u)^{-d/2}\, e^{-R^2/2u} [-2(1-u)]^{i-1}, \qquad i = 1, 2, 3 \tag{4.5c}$$

We conclude that, at least for the model $K_{ij} = 1$, a relatively simple scaling behavior emerges in the scaling limit. Note that the scaling behavior occurs in the product space $(m, n, \mathbf{r})$, and that it holds for general initial conditions.

5. THE TWO-TIME CORRELATION FUNCTIONS

I restrict consideration to monodisperse initial conditions. The correlation function κ_{nm}, or, rather, its Fourier transform $\hat{\kappa}_{nm}$, is determined by Eq. (1.5). To solve this equation with $K_{ij}=1$ and $D_k=D$ I introduce new functions

$$a_{nm}(\mathbf{q};t,t_1)\equiv\hat{\kappa}_{nm}(\mathbf{q};t,t_1)\,e^{Dq^2(t-t_1)} \tag{5.1}$$

satisfying

$$\frac{\partial}{\partial t}a_{nm}(\mathbf{q};t,t_1)=\sum_{j=1}^{\infty}A_{nj}a_{jm}(\mathbf{q};t,t_1) \tag{5.2}$$

The initial condition for a_{nm} at $t=t_1$ is the same as for $\hat{\kappa}_{nm}$ [see (1.5b)].

The problem (5.2), with A_{nj} given in (1.3b) and $K_{ij}=1$, has already been solved in ref. 7. The solution is that a_{nm} is *linearly* related to its initial value at $t=t_1$, i.e.,

$$a_{nm}(\mathbf{q};t,t_1)=\sum_{j=1}^{\infty}Y_{nj}(t,t_1)\,a_{jm}(\mathbf{q};t_1,t_1) \tag{5.3}$$

where the evolution matrix Y_{nj} is given by

$$Y_{nj}(t,t_1)=Q_{n-j}(t,t_1)-Q_n(t,t_1) \tag{5.4a}$$

$$\begin{aligned}Q_n(t,t_1)=&(1+\tfrac{1}{2}t_1)^2(n+1)\,c_{n+1}(t)-t_1(1+\tfrac{1}{2}t_1)\,nc_n(t)\\&+(\tfrac{1}{2}t_1)^2(n-1)\,c_{n-1}(t)\end{aligned} \tag{5.4b}$$

We recall that the matrix Y_{nj} has the properties

$$\sum_{j=1}^{\infty}Y_{nj}(t,t_1)\,jc_j(t_1)=nc_n(t)-Q_n(t,t_1) \tag{5.5a}$$

$$\sum_{j=1}^{\infty}Y_{nj}(t,t_1)\,c_j(t_1)=R_n(t,t_1) \tag{5.5b}$$

where $R_n(t,t_1)$ is given by

$$R_n(t,t_1)=-\tfrac{1}{2}[(2+t_1)(t-2n)/(2+t)+t_1(2n-2-t)/t]\,c_n(t) \tag{5.6}$$

Combination of (5.1) and (5.3)–(5.5) with the initial condition (1.5b) of $\hat{\kappa}_{nm}$ and the explicit form (3.2) of F_{mn} finally yields the following impressive expression for the (Fourier-transformed) correlation functions $\hat{\kappa}_{nm}$:

$$\begin{aligned}\hat{\kappa}_{nm}(\mathbf{q};t_2,t_1)=e^{-Dq^2(t_2-t_1)}\{&[\alpha_1(\mathbf{q},t_1)+m\alpha_2(\mathbf{q},t_1)]\,R_n(t_2,t_1)\\&+[\alpha_2(\mathbf{q},t_1)+m\alpha_3(\mathbf{q},t_1)][nc_n(t_2)-Q_n(t_2,t_1)]\\&+Y_{nm}(t_2,t_1)\}\,c_m(t_1)\end{aligned} \tag{5.7}$$

where $\boldsymbol{\alpha}(\mathbf{q}, t)$ is given in (3.2b). This result for $\hat{\kappa}_{nm}$ may readily be inverted to yield an explicit expression for the two-time correlation functions $\kappa_{nm}(\mathbf{r}; t_2, t_1)$. The outcome has the same form as in (5.7), but $\alpha_i(\mathbf{q}, t_1)$ $\exp[-Dq^2(t_2-t_1)]$ is replaced by $A_i(\mathbf{r}; t_2, t_1)$, which is defined as

$$\mathbf{A}(\mathbf{r}; t_2, t_1) = \mathit{\Lambda}(t_1)\cdot\mathbf{B}(\mathbf{r}; t_2, t_1) \tag{5.8a}$$

$$B_i(\mathbf{r}; t_2, t_1) = \delta_{i1}\, g[\mathbf{r}; 2D(t_1+t_2)] + \int_0^{t_1} d\tau\, (-\tau/2)^{i-1} g[\mathbf{r}; 2D(t_1+t_2-2\tau)] \tag{5.8b}$$

and the bare factor $\exp[-Dq^2(t_2-t_1)]$ (which multiplies Y_{nm}) is replaced by $g[\mathbf{r}; 2D(t_2-t_1)]$.

6. FLUCTUATIONS IN THE DENSITY

A quantity of considerable physical interest that deserves a separate discussion is the fluctuation in the mass density. The correlations at *different* times are described by the two-time correlation function

$$\rho(\mathbf{r}; t_2, t_1) \equiv \sum_{m,n} mn\kappa_{mn}(\mathbf{r}; t_2, t_1), \qquad t_2 \geqslant t_1 \tag{6.1}$$

The equal-time correlation function $\rho(\mathbf{r}, t)$ is obtained from (6.1) by setting $t_2 = t_1 = t$. The Fourier transforms of $\rho(\mathbf{r}; t_2, t_1)$ and $\rho(\mathbf{r}, t)$ will be denoted by $\hat{\rho}(\mathbf{q}; t_2, t_1)$ and $\hat{\rho}(\mathbf{q}, t)$, respectively.

There exists a very simple relation between the Fourier transforms $\hat{\rho}(\mathbf{q}; t_2, t_1)$ and $\hat{\rho}(\mathbf{q}, t)$, provided that $D_k = D$. This may be seen from (1.5a) by multiplying with mn and summing over all m and n. The result is

$$\frac{\partial}{\partial t}\hat{\rho}(\mathbf{q}; t, t_1) = -Dq^2\hat{\rho}(\mathbf{q}; t, t_1) \tag{6.2}$$

which may readily be integrated to yield

$$\hat{\rho}(\mathbf{q}; t_2, t_1) = e^{-Dq^2(t_2-t_1)}\hat{\rho}(\mathbf{q}, t_1) \tag{6.3}$$

Similarly, one can derive a simple expression for $\hat{\rho}(\mathbf{q}, t)$ if one uses the relation between $\hat{\rho}(\mathbf{q}, t)$ and $F_{mn}(\mathbf{q}, t)$, i.e.,

$$\hat{\rho}(\mathbf{q}, t) = \sum_{m,n} mn[F_{mn}(\mathbf{q}, t) + \delta_{mn} c_m(t)] \tag{6.4}$$

It follows from (1.3) that

$$\frac{\partial}{\partial t}\hat{\rho}(\mathbf{q},t) = -2Dq^2[\hat{\rho}(\mathbf{q},t) - M_2(t)] \tag{6.5}$$

where $M_2(t) = \sum_{k=1}^{\infty} k^2 c_k(t)$ is the second moment of $c_k(t)$. Equation (6.5) has the solution

$$\hat{\rho}(\mathbf{q},t) = M_2(0)(1 - e^{-2Dq^2 t}) + \int_0^t dt'\, \dot{M}_2(t')[1 - e^{-2Dq^2(t-t')}] \tag{6.6}$$

Fourier inversion of (6.6) yields an expression for $\rho(\mathbf{r},t)$,

$$\begin{aligned}\rho(\mathbf{r},t) = {} & -M_2(0)\, g(\mathbf{r}; 4Dt) \\ & - \int_0^t dt'\, \dot{M}_2(t')\, g(\mathbf{r}; 4D(t-t')) + M_2(t)\, \delta(\mathbf{r})\end{aligned} \tag{6.7}$$

Similarly one finds from (6.3), in combination with (6.6), that

$$\begin{aligned}\rho(\mathbf{r}; t_2, t_1) = {} & -M_2(0)\, g(\mathbf{r}; 2D(t_2+t_1)) \\ & - \int_0^{t_1} dt'\, \dot{M}_2(t')\, g(\mathbf{r}; 2D(t_2+t_1-2t')) \\ & + M_2(t)\, g(\mathbf{r}; 2D(t_2-t_1))\end{aligned} \tag{6.8}$$

Here $g(\mathbf{r}; \sigma^2)$ is the Gaussian distribution, defined in (3.5). I stress that Eqs. (6.2)–(6.8) are *generally valid*, provided that $D_k = D$, i.e., these equations hold for general reaction kernels K_{ij} and general initial conditions.

Next I specialize for $K_{ij} = 1$, and consider the limit of large times. This limit is of particular interest, since one expects that the density fluctuations become large as $t \to \infty$. In addition, we keep $\theta = 2Dq^2 t$ fixed. Since for $K_{ij} = 1$ (and general initial conditions) it holds that $\dot{M}_2(t) = 1$ (all $t > 0$), it follows from (6.6) that the density fluctuations increase *linearly* in time as $t \to \infty$:

$$\hat{\rho}(\mathbf{q},t) \xrightarrow{\text{S}} t(\theta - 1 + e^{-\theta})/\theta \tag{6.9}$$

This shows that, at large times, the density fluctuations diverge at all length scales. I remark that this conclusion, that the density fluctuations diverge as $t \to \infty$, holds quite generally for any nongelling model K_{ij}. This follows from (6.6) or (6.7): the only requirement is that $M_2(t)$ diverges as $t \to \infty$, which happens in any nontrivial model for irreversible aggregation.

7. EXTENSIONS

How special is the model (1.6) discussed in this paper? To investigate this question, concentrate on the scaling laws found in Section 4 and consider the large class of models with the property that the rate constants $K(i, j)$ are homogeneous functions of the cluster sizes: $K(i, j) = a^{-\lambda}K(ai, aj)$ for all $a > 0$. Could it be that scaling laws like (4.3a), (4.5a) are generally valid for such homogeneous kernels?

First consider the case where the diffusion constants are given by $D_k = D$ for all k. In this case it is relatively easy to show, along the lines of ref. 7, Section 7.2, that the scaling behavior (4.3a), (4.5a) with $\theta = 2Dq^2t$ is indeed consistent for all nongelling homogeneous kernels with $\lambda < 1$. Note that this scaling behavior occurs in the product space $(m, n, \mathbf{q})$ or $(m, n, \mathbf{r})$. For the nongelling models with $\lambda = 1$ and the gelling models with $\lambda > 1$ the result is very simple. In this case $F_{mn} \to e_{mn}(t)$, or $E_{mn} \to e_{mn}(t)\,\delta(\mathbf{r})$, where e_{mn} are the nonspatial factorial cumulants. Thus, for $\lambda \geqslant 1$, all correlations become local in the scaling limit. These results for $\lambda \geqslant 1$ may be verified explicitly on two exactly soluble models,(2) namely $K_{ij} = ij$ and $K_{ij} = i + j$.

Next consider the case of general diffusion constants D_k, where we assume that $D_k \sim Dk^{-\alpha}$ as $k \to \infty$ for some $\alpha \geqslant 0$. In this case one finds the *same* scaling laws (4.3a), (4.5a) if $\lambda < 1$, provided that the scaling variable θ is replaced by $\theta_\alpha \equiv 2Dq^2t/[s(t)]^\alpha$. The result for $\lambda \geqslant 1$ remains unchanged.

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