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Cluster size distribution in irreversible aggregation at large times

P G J van Dongen and M H Ernst

Institute for Theoretical Physics, Princetonplein 5, PO Box 80.006, 3508 TA Utrecht, The Netherlands

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Abstract. We assume that the size distribution $c_k(t)$ satisfies Smoluchowski's coagulation equation with rate coefficients $K(i,j)$, behaving as $K(i,j) \sim i^\mu j^\nu$ $(i \ll j)$, and find the following: in gelling and non-gelling systems of class I $(\mu > 0)$ the general solution $c_k(t)$ approaches for $t \to \infty$ the exact solution Cb_k/t $(k = 1, 2, \ldots)$, where the b_k's are independent of the initial conditions $c_k(0)$, and can be determined from a recursion relation. In class II systems $(\mu = 0)$, $c_k(t)/c_1(t) \to b_k$ $(t \to \infty, k = 1, 2, \ldots,)$, but the b_k's depend on $c_k(0)$. Only in the scaling limit ($k \to \infty$, $s(t) \to \infty$ with $k/s(t) =$ finite; $s(t)$ is the mean cluster size) does $c_k(t)$ approach a form independent of the initial distribution. Class III, where $c_k(t)/c_1(t) \to \infty$ $(t \to \infty, k = 2, 3, \ldots)$ has not been considered here.

1. Introduction

One of the main problems in the theory of irreversible aggregation is to determine the long time behaviour of the cluster size distribution $c_k(t)$ $(k = 1, 2, \ldots)$, which is assumed to be described by Smoluchowski's equation:

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} K(i,j) c_i c_j - c_k \sum_{j=1}^{\infty} K(k,j) c_j. \tag{1.1}$$

The coagulation coefficients $K(i,j)$ describe the rate at which i-clusters and j-clusters coalesce.

As most coagulation kernels $K(i,j)$, used in the literature (e.g. Drake 1972, White 1982) are homogeneous functions of i and j, at least for large cluster sizes, we restrict ourselves to such kernels and characterise $K(i,j)$ by exponents describing their i and j dependence at large i and j:

$$K(ai, aj) = a^\lambda K(i,j) \tag{1.2}$$

$$K(i,j) \simeq i^\mu j^\nu \qquad j \gg i, \lambda = \mu + \nu \tag{1.3}$$

$$K(x, 1-x) \simeq x^\mu \{1 + K_1 x^{\mu'} + \ldots\} \qquad x \to \infty, \mu' > 0. \tag{1.4}$$

The case $\mu > 0$ will be referred to as class I, $\mu = 0$ as class II, and $\mu < 0$ as class III. In class I and class III the rate constants for reactions of large with large, respectively large with small, clusters are dominant. In the intermediate class II the rate constants $K(i,j)$ for aggregation of large with large and small with large clusters are of equal size. The reactivity of large clusters should not increase faster than their size; thus

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$\lambda \leqslant 2$, $\nu \leqslant 1$, but no restrictions are imposed on μ. It was further shown (e.g. Ernst *et al* 1982) that $\lambda > 1$ corresponds to gelling, and $\lambda < 1$ to non-gelling processes. Equation (1.4) gives a more detailed specification of the kernels, required in our later discussions. We remark that our results will be valid not only for exactly homogeneous kernels (1.2), but also for asymptotically homogeneous kernels, with the property $K(i,j) \simeq \chi(i,j)$ $(i, j \gg 1)$, where $\chi(i,j) \equiv \lim_{a\to\infty} a^{-\lambda} K(ai, aj)$ is a homogeneous function satisfying (1.2), (1.3) and (1.4).

To discuss long time properties two different methods have been used in the literature, which lead to partially complementary and sometimes conflicting results. One method uses scaling functions (Friedlander 1977, Leyvraz and Tschudi 1982); the other one a recursion relation (Ziff *et al* 1982, Leyvraz 1984). The scaling function method (SFM) describes the dominant time dependence at large t, whereas the recursion relation method (RRM) only gives the limiting value of $c_k(t)/c_1(t)$ as $t \to \infty$, but not the approach towards this value. On the other hand, the SFM makes only predictions about large k values, whereas the RRM makes predictions about all k values.

In the recursion relation method one has been looking for asymptotic solutions of the form $c_k(t)/c_1(t) \to b_k$ $(k = 1, 2, \ldots)$ as $t \to \infty$ in non-gelling systems (Leyvraz 1984), where the b_k's are independent of $c_k(0)$, and for a special post-gelation solution of the form $c_k(t) = c_1(t) b_k$ $(k = 1, 2, \ldots)$ in gelling systems (Ziff *et al* 1982). In all these cases the b_k's are determined by the same recursion relation.

In the scaling function method for non-gelling systems ('theory of self-preserving spectra') one assumes that the size distribution approaches for large t *and* large k a scaling form $c_k(t) \sim s^{-2}\varphi(k/s)$, where $s(t)$ is the mean cluster size, increasing as $s(t) \sim t^z$ $(t \to \infty)$. The scaling ansatz, combined with Smoluchowski's equation, yields a nonlinear integral equation for the scaling function $\varphi(x)$. In gelling systems the solution of Smoluchowski's equation approaches only a scaling form as t approaches the gel point t_c from below. As we are interested in the long time behaviour, the scaling function method does not give much useful information here.

The purpose of this paper is (i) to show that the recursion relation method is describing the long time behaviour of $c_k(t)$ for general initial distributions in gelling and non-gelling systems of class I, and (ii) to show that the recursion relation method is not correct for class II and III systems.

In point (i) we extend (see § 3) the results of Leyvraz for the special kernel $K(i,j) = (ij)^\omega$ $(0 < \omega < \frac{1}{2})$ to general homogeneous kernels of non-gelling class I systems. For gelling systems we have two types of new results in § 4. In the literature only the special post-gelation solution, $c_k(t) = b_k c_1(t)$ for $t \geqslant t_c$, has been considered for a few special coagulation kernels, in particular for $K(i,j) = (ij)^\omega$ $(\frac{1}{2} < \omega \leqslant 1)$ (Leyvraz and Tschudi 1982, Ziff *et al* 1982). In this paper the special solution is extended to all homogeneous kernels of class I. Furthermore, we show that the solution $c_k(t)$ for *general initial conditions* approaches the special post-gelation solution as $t \to \infty$. The large k behaviour of b_k obtained from this method is in agreement with the results of the scaling function method for non-gelling class I systems.

Regarding point (ii) we shall see that $c_k(t)/c_1(t) \to \infty$ as $t \to \infty$ in class III, and that in class II, $c_k(t)/c_1(t)$ $(k = 1, 2, \ldots)$ does in general approach a finite constant as $t \to \infty$. However, the constants depend on the initial distribution and cannot be determined from the recursion relation method (see § 4). This result disproves an earlier result of Leyvraz (1984) for the special class II kernel $K(i,j) = i^\lambda + j^\lambda$ $(0 < \lambda < 1)$, which was in conflict with the predictions of the scaling function method, as was shown by van Dongen and Ernst (1985b).

In § 5 we explicitly show for a few examples that the values for the τ exponent, defined as $b_k \sim k^{-\tau}$ ($k \to \infty$), are different in the scaling function—and the recursion relation method.

We start our discussion in § 2 by reviewing the derivation of the recursion relation, and show that it contains an implicit assumption, which is fulfilled in class I (see § 3) and violated in class II (see § 4). In order to test the implicit assumption for class II systems, we require some results from the scaling function method obtained by van Dongen and Ernst (1985a), which are summarised in appendix 1.

2. Derivation of the recursion relation

We review the derivation of the recursion relation, that has been used in two different contexts: gelling and non-gelling systems.

First we consider *gelling systems*. Here there exists a special post-gel solution $c_k(t) = c_1(t) b_k$ ($k = 1, 2, \ldots$), where the b_k's satisfy a recursion relation. One of the main goals of this paper is to show that the size distribution in gelling systems for arbitrary initial distributions shows universal behaviour, independent of $c_k(0)$, namely it approaches the special solution, in the following sense

$$\lim_{t\to\infty} c_k(t)/c_1(t) = b_k \tag{2.1}$$

where b_k ($k = 1, 2, \ldots$) are bounded positive numbers with $b_1 = 1$.

First we derive the recursion relation for b_k. We start with the observation of Ziff *et al* (1982) that the coagulation equation (1.1) admits an exact solution with a simple time dependence $c_k(t) = c_k(t_c)/[1+\beta(t-t_c)] \equiv b_k c_1(t)$, where $b_k = c_k(t_c)/c_1(t_c)$ ($k = 1, 2, \ldots$) are positive numbers and β and t_c unknown constants. It corresponds to a special set of initial conditions $c_k(0)$. Inserting this solution into (1.1) yields

$$-(\beta/c_1(t_c))b_k = \tfrac{1}{2} \sum_{i+j=k} K(i,j) b_i b_j - b_k \sum_{j=1}^{\infty} K(k,j) b_j. \tag{2.2}$$

The unknown β may be eliminated using (2.2) for $k = 1$, and the following recursion relation results

$$R(b_k) \equiv \tfrac{1}{2} \sum_{i+j=k} K(i,j) b_i b_j - b_k \sum_{j=1}^{\infty} (K(k,j) - K(1,j)) b_j = 0 \tag{2.3}$$

where b_k ($k = 1, 2, \ldots$) are positive numbers and $b_1 = 1$. This exact solution has the remarkable property

$$M(t) = \sum_{k=1}^{\infty} k c_k(t) = M(t_c)/[1+\beta(t-t_c)] \tag{2.4}$$

i.e. the total mass, contained in finite size clusters decreases in time for $t > t_c$. Therefore we are necessarily dealing with gelling systems ($\lambda > 1$), where the above $c_k(t_c)/[1+\beta(t-t_c)]$ represents a post-gelation solution, describing a phase with a non-vanishing gel fraction $G(t) = 1 - M(t)$, and t_c may be identified as the gel point.

As we shall show later on, the solution b_k of the recursion relation at large k, has algebraic k-dependence, i.e.

$$b_k \simeq Bk^{-\tau} \qquad k \to \infty. \tag{2.5}$$

This relation defines the τ exponent obtained from the recursion relation, which is the quantity of main interest in this paper. Since the total mass is conserved, $\Sigma\, kc_k(t) = 1$, below the gel point $(t \leq t_c)$,we have $1 = \Sigma\, kc_k(t_c) \sim \Sigma\, kb_k$ which implies $\tau > 2$. It turns out that the *exact solution* $c_k(t) = b_k/(\alpha + \beta t)$ in non-gelling systems $(\lambda < 1)$ corresponds to an infinite sol mass, $\Sigma\, kc_k(t) \sim (\alpha + \beta t)^{-1} \Sigma\, kb_k \to \infty$ since $\tau < 2$. This solution is therefore physically unacceptable. However, *asymptotic solutions* of the form $c_k(t) \simeq c_1(t) b_k$ $(t \to \infty)$ could be physically acceptable in non-gelling systems, because $c_k(t)/c_1(t)$ may approach b_k non-uniformly in k, so that $\Sigma\, kc_k(t) = 1$, whereas $\Sigma\, kb_k \to \infty$ since $\tau < 2$.

Next, we turn to *non-gelling systems*. Here Leyvraz has argued that Smoluchowski's equation for the product kernel $K(i,j) = (ij)^\omega$ $(0 < \omega < \frac{1}{2}$; class I) and sum kernel $K(i,j) = i^\omega + j^\omega$ $(0 < \omega < 1$; class II) admits an asymptotic solution of the form (2.1), where the b_k's are independent of the initial distribution, and determined by the recursion relation (2.3). A second goal of this paper is to extend Leyvraz's result to coagulation kernels of class I and to show that the recursion relation method is not valid for class II and III kernels.

As a criterion to decide whether asymptotic solutions of the form (2.1) are possible for the kernel $K(i,j)$ under consideration, we use the results from the scaling function method. In this context the most important results are (see appendix 1): $\varphi(x) \sim \exp(-x^{-|\mu|})(x \to 0)$ in aggregation processes of class III $(\mu < 0)$, and $\varphi(x) \sim x^{-\tau}$ $(x \to 0)$ in class I and II. These results have the following implications for the size distribution starting from general initial distributions: in class III systems, $c_k(t)/c_j(t) \to \infty$ $(t \to \infty$; $k > j$; k, j fixed, but large), and in all non-gelling systems of class I and II, $c_k(t)/c_j(t) \sim (j/k)^\tau =$ constant $(t \to \infty$; k, j fixed, but large). Thus, class III processes do not admit solutions, satisfying (2.1). We, therefore, concentrate on class I and class II systems. If we make the additional assumption that the last asymptotic relation holds for *all* $j = 1, 2, \ldots,$ then one would have to look in class I and II for asymptotic solutions with property (2.1).

The next question to be decided for gelling and non-gelling systems is whether the asymptotic solution b_k in (2.1) can be determined from the recursion relation (2.3). Following Leyvraz we introduce $\nu_k(t) \equiv c_k(t)/c_1(t)$ and substitute it into the coagulation equation (1.1) with the result:

$$(1/c_1)\, \mathrm{d}\nu_k/\mathrm{d}t = R(\nu_k). \tag{2.6}$$

As one is interested in those systems for which $\nu_k(t)$ approaches a constant b_k, the LHS of (2.6) is set equal to zero, and the ν_k equation reduces to the long time recursion relation, $R(b_k) = 0$. However, the LHS of (2.6) does not necessarily approach zero, since in irreversible aggregation $c_1(t) \to 0$ as $t \to \infty$. Implicitly one has therefore made the additional assumption

$$(1/c_1(t))\, \mathrm{d}\nu_k/\mathrm{d}t \to 0 \qquad t \to \infty. \tag{2.7}$$

The question whether this assumption is satisfied, i.e. whether the recursion relation (2.3) has any bearing on the factors b_k, will be discussed for class I systems in § 3, and for class II systems in § 4.

3. Class I systems

3.1. Non-gelling systems

In this section we argue that the limiting ratio $b_k = \lim_{t\to\infty} c_k/c_1$ for non-gelling models ($\lambda < 1$) of class I ($\mu > 0$) satisfies the recursion relation (2.3) provided the b_k's satisfy the strict inequalities:

$$E_1 < E_k < \infty \qquad k = 2, 3, \ldots. \tag{3.1}$$

Here we have defined

$$E_k = \lim_{t\to\infty} \sum_{j=1}^{\infty} K(k,j)c_j/c_1 = \sum_{j=1}^{\infty} K(k,j)b_j \tag{3.2}$$

where it is assumed that the infinite sums converge. The condition $E_k > E_1$ ($k = 2, 3, \ldots$) is trivially fulfilled if $K(1,j) < K(k,j)$. Cases where the inequalities (3.1) are not fulfilled will be discussed at the end of this section.

In order to show that Smoluchowski's equation reduces to the recursion relation (2.3) as $t \to \infty$, we introduce

$$\sigma_k(t) = \sum_{j=1}^{\infty} K(k,j)c_j(t), \qquad S_k(t) = \int_0^t \mathrm{d}t'\, \sigma_k(t') \tag{3.3}$$

and solve the kinetic equation (1.1) with the result

$$c_k(t) = \exp[-S_k(t)]\left(c_k(0) + \int_0^t \mathrm{d}t'\, \tfrac{1}{2} \sum_{i+j=k} K(i,j)c_i(t')c_j(t') \exp[S_k(t')]\right). \tag{3.4}$$

The long time behaviour of $S_k(t)$ can be determined from $c_1(t)$ ($t \to \infty$), which in turn is given by (1.1) for $k = 1$:

$$\dot{c}_1 = -c_1\sigma_1 \simeq -(c_1)^2 E_1 \qquad t \to \infty \tag{3.5}$$

provided $E_1 < \infty$. Thus, we have in (3.3) as $t \to \infty$:

$$\sigma_k(t) \simeq c_1(t)E_k \simeq E_k/(E_1 t) \tag{3.6}$$

$$S_k(t) \simeq (E_k/E_1) \log t \tag{3.7}$$

provided $E_k < \infty$. With the help of (3.6) and (3.7) the dominant long time behaviour of the t integral in (3.4) can be estimated as $t^{-\alpha(k)}$ with $\alpha(k) = -1 + E_k/E_1$. This quantity diverges as $t \to \infty$ since $E_k > E_1$. Thus, $c_k(0)$ may be neglected in (3.4), and the equation reduces to the long time form

$$\int_0^t \mathrm{d}t'\, \tfrac{1}{2} \sum_{i+j=k} K(i,j)c_i(t')c_j(t') \exp[S_k(t')] \simeq b_k c_1(t) \exp[S_k(t)]. \tag{3.8}$$

After differentiation of (3.8), yielding

$$\tfrac{1}{2} \sum_{i+j=k} K(i,j)c_i(t)c_j(t) \simeq b_k(\sigma_k c_1 + \dot{c}_1) \qquad t \to \infty \tag{3.9}$$

we obtain, using (2.1), (3.5), (3.6) and (3.7):

$$\tfrac{1}{2} \sum_{i+j=k} K(i,j)b_i b_j = (E_k - E_1)b_k \tag{3.10}$$

which is in fact the recursion relation (2.3), $R(b_k) = 0$ with $b_1 = 1$. The cluster size distribution behaves as $c_k(t) \sim c_1(t) b_k \sim C b_k / t$ ($k = 1, 2, \ldots, t \to \infty$), where $C b_k / t$ is an exact, but unphysical solution of Smoluchowski's equation containing infinite mass. Thus, in non-gelling systems of class I, satisfying the inequalities (3.1), the factors b_k obey the recursion relation (2.3). This implies in particular that in such systems the assumption (2.7) is correct.

In order to determine the asymptotic solution of the recursion relation, we multiply (2.3) with k, and sum over k to obtain the following representation of the recursion relation:

$$E_1 \sum_{j=1}^{k} j b_j = \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} i K(i,j) b_i b_j. \tag{3.11}$$

Next we substitute the asymptotic form (2.5) into (3.11). In non-gelling class I models, one finds a consistent solution only if one assumes that $\tau < 2$. In this case (3.11) reduces to

$$B E_1 k^{2-\tau} / (2-\tau) \simeq B^2 k^{3+\lambda-2\tau} \int_0^1 \mathrm{d}x \int_{1-x}^{\infty} \mathrm{d}y \, x K(x,y) (xy)^{-\tau} \qquad k \to \infty. \tag{3.12}$$

Comparison of the dominant orders in k gives $\tau = 1 + \lambda$ in agreement with the result from the scaling function method and consistent with the assumption (3.1), i.e. $E_k < \infty$. The special case, $\lambda = 1$, leads to $b_k \sim k^{-2} \log k$, which is more complicated and will not be discussed here.

So far the general results. In special cases, e.g. when no monomers are present in the system ($c_1(0) = 0$), or when the conditions (3.1) are violated, results different from (2.1) will be found. As an example we have considered in appendix 2 a system where dimers, instead of monomers, are least reactive, i.e. $K(2,j) < K(1,j)$ and $K(2,j) < K(k,j)$ ($k > 2; j \geq 1$) and $c_2(0) \neq 0$. Even if $c_1(0) \neq 0$, one finds that $c_k(t) \sim t^{-\beta(k)}$ ($t \to \infty$), with $\beta(2n) = 1$ and $\beta(2n-1) > 1$ ($n = 1, 2, \ldots$). In the final stages of the aggregation process all odd cluster sizes have disappeared from the system, and only even cluster sizes remain. The limiting ratio $b_k \equiv \lim_{t \to \infty} c_k(t)/c_2(t)$ satisfies a recursion relation similar to (2.3), namely

$$\tfrac{1}{2} \sum_{i+j=k} K(i,j) b_i b_j = b_k \sum_{j=1}^{\infty} (K(k,j) - K(2,j)) b_j \tag{3.13}$$

which is to be solved subject to the initial conditions $b_1 = 0$, $b_2 = 1$. As one sees, $b_k \neq 0$ only for $k =$ even, and b_{2n} behaves asymptotically as $b_{2n} \sim n^{-\tau}$ with $\tau = 1 + \lambda$. The cluster size distribution approaches again the exact, but unphysical solution $c_k(t) = c_2(t) b_k = C b_k / t$ ($k = 1, 2, \ldots$), with b_k determined by (3.13). Included in this example is the special case where $c_1(0) = 0$ (and possibly $K(1,j) < K(2,j)$, as the monomeric rate constants are irrelevant in a system without monomers).

The previous example may be generalised to a situation where l-mers are least reactive, $K(l,j) < K(k,j)$ ($k \neq l; j = 1, 2, \ldots$), and $c_l(0) \neq 0$. In this case the outcome is that multiples of l-mers are the only surviving species in the final stages of the aggregation process.

3.2. Gelling systems

As we are interested in the long time behaviour of $c_k(t)$ in gelling systems of class I ($\mu > 0; \lambda > 1$), we are necessarily dealing with post-gel solutions. A characteristic property of a post-gel solution is that it carries a non-vanishing mass flux $\dot{M}^{(k)}$ ($k \to \infty$)

transferring clusters with sizes $<k$ to those with sizes $>k$, in the limit as $k\to\infty$. This is the cascading growth process by which sol particles are transformed into gel. According to Leyvraz and Tschudi (1982) and van Dongen and Ernst (1985a) the mass flux is

$$\dot{M}^{(\infty)}(t)=-\lim_{k\to\infty}\sum_{i=1}^{k}\sum_{j=k-i+1}^{\infty} iK(i,j)c_ic_j. \tag{3.14}$$

It must be finite and non-vanishing at all times $t>t_c$, where t_c is the gel point. The RHS of (3.14) can only be non-vanishing if $c_k(t)$ has a sufficiently slow (algebraic) decay at large k, i.e. if $c_k(t)\simeq A(t)k^{-\tau}$ $(k\to\infty)$. Thus,

$$\dot{M}^{(\infty)}(t)=-A^2(\lim_{k\to\infty}k^{3+\lambda-2\tau})\int_0^1 \mathrm{d}x\int_{1-x}^{\infty}\mathrm{d}y\,xK(x,y)(xy)^{-\tau} \tag{3.15}$$

is bounded and non-zero only if $\tau=\frac{1}{2}(\lambda+3)$. This implies again $c_k(t)/c_j(t)\simeq(k/j)^{-\tau}$ $(k,j\gg 1)$. We therefore make the assumption (2.1) that positive constants $b_k<\infty$ exist such that $c_k/c_1\to b_k$ $(t\to\infty)$ for general initial distributions. The asymptotics $(k\to\infty)$ of b_k are then given by (2.5) with $\tau=\frac{1}{2}(\lambda+3)$.

The assumption (2.1) in gelling systems is supported by the exactly solvable model $K(i,j)=ij$, with $\lambda=2$. In this case one finds (Ziff *et al* 1983) the exact post-gel solution $(t>t_c=1)$: $c_1(t)=1/et$ and $c_k(t)/c_1(t)=b_k=k^{k-2}e^{1-k}/k!$ with $b_k\simeq ek^{-5/2}/(2\pi)^{1/2}$ $(k\to\infty)$ corresponding to the special monodisperse initial distribution and one can show for general initial distributions $c_k(0)$ that $c_k(t)/c_1(t)\simeq b_k(1+\mathrm{O}(t^{-2}))$ as $t\to\infty$, where the leading term is independent of $c_k(0)$. The $\mathrm{O}(t^{-2})$ correction term depends upon the initial conditions via $c_1(0)$, $c_2(0)$ and $c_3(0)$.

The validity of the recursion relation, $R(b_k)=0$, for general initial conditions can be shown using virtually the same arguments as in the previous section. They will not be repeated here. In order to determine the asymptotic solutions b_k $(k\to\infty)$ of $R(b_k)=0$, or equivalently of (3.11), we insert the ansatz $b_k\simeq Bk^{-\tau}$ $(k\to\infty)$ into (3.11), with the result

$$E_1\sum_{j=1}^{\infty} jb_j=B^2(\lim_{k\to\infty}k^{3+\lambda-2\tau})\int_0^1\mathrm{d}x\int_{1-x}^{\infty}\mathrm{d}y\,xK(x,y)(xy)^{-\tau}. \tag{3.16}$$

We conclude that $\tau=\frac{1}{2}(\lambda+3)$, in agreement with the τ exponent in the scaling function method.

In summary, for gelling systems we have shown in this subsection that the solutions of Smoluchowski's equation for general initial distributions converge for long times to the exact post-gel solution $c_k(t)=c_1(t)b_k$, of $c_k(t)/c_1(t)\simeq b_k$ $(k=1,2,\ldots;t\to\infty)$.

The examples, given in the previous section, where the conditions (3.1) are not fulfilled, are equally relevant for gelling and non-gelling systems.

4. Class II disproof of the recursion relation

The arguments of § 3, leading to the recursion relation (2.3), break down because the first and/or the second inequality in (3.1) is violated. $E_k=\Sigma_{j=1}^{\infty}K(k,j)b_j$ in (3.1) and (3.2) is divergent in class II since $\tau<1+\lambda$ (see below (A1.4)). As we shall see, the ratio $c_k(t)/c_1(t)$ as $t\to\infty$ in class II aggregation processes does not approach universal behaviour, independent of the initial distribution. Consequently, the asymptotic property (2.1) with $c_k(t)/c_1(t) \to b_k$ ($t \to \infty$; $k = 1, 2, \ldots$) with b_k determined by the recursion relation (2.3) does not hold.

Before presenting the general arguments we briefly discuss two special examples of class II processes without universal long time behaviour. First, we consider the kernel $K(i,j) = i+j$, for which Smoluchowski's equation can be solved exactly (Golovin 1963, Ziff *et al* 1984). To illustrate our point it is sufficient to solve (1.1) for $k=1$ and $k=2$, yielding

$$\begin{aligned} c_1(t) &= c_1(0)\exp\{-[t+M_0(0)(1-e^{-t})]\} \\ c_2(t) &= [c_2(0)+c_1^2(0)(1-e^{-t})]\exp\{-[t+2M_0(0)(1-e^{-t})]\} \end{aligned} \tag{4.1}$$

and calculate the following limits of $\nu_k = c_k/c_1$:

$$\begin{aligned} &\lim_{t\to\infty} \nu_2(t) = b_2 = [c_1(0) + c_2(0)/c_1(0)]\exp[-M_0(0)] \\ &\lim_{t\to\infty} (1/c_1(t))\dot{\nu}_2(t) = 1 - M_0(0)[1 + c_2(0)/c_1^2(0)]. \end{aligned} \tag{4.2}$$

Thus the b_k's still depend on the initial distribution, and the LHS of (4.2), namely $(1/c_1)\dot{\nu}_k \to$ constant ($t\to\infty$, $k = 2, 3, \ldots$), only vanishes for the special monodisperse initial condition, $c_k(0) = \delta_{k1}$, which is the only case for which the recursion relation is correct. Next, we consider the special example of the sum kernel $K(i,j) = i^\lambda + j^\lambda$ ($0 < \lambda < 1$), for which van Dongen and Ernst (1985b) have shown that the additional assumption (2.7) is violated and the value (Leyvraz 1984) for the τ exponent, $\tau_R = 1 + \frac{1}{2}\lambda$, as obtained from the recursion relation, is in general incorrect.

For general class II processes we follow the same procedure as for the sum kernel, i.e. we try to estimate the long time behaviour of LHS (2.6) under the assumption that the size distribution is described by the scaling ansatz, $c_k(t) \sim t^{-2z}\varphi(kt^{-z})$. This requires the explicit form of the scaling function $\varphi(x)$ as predicted by Smoluchowski's equation. With that result, we are able to show that the LHS of (2.6) approaches a constant or diverges as $t \to \infty$. In either case the recursion relation is irrelevant for the description of the long time behaviour of $c_k(t)$ in aggregation processes of class II. The details go as follows. We represent the approach of $\nu_k(t) = c_k(t)/c_1(t)$ to its limiting form b_k as $\nu_k \simeq b_k\psi(kt^{-z})$ with $\psi(0) = 1$. For large k, where $b_k \simeq Bk^{-\tau}$ ($k\to\infty$) this representation is simply a different form of the scaling ansatz with $\varphi(x) = Bx^{-\tau}\psi(x)$, so that

$$c_k \sim t^{-2z}\varphi(kt^{-z}) \sim k^{-\tau}t^{-\gamma}\psi(kt^{-z}) \qquad k,\ t \text{ large} \tag{4.3}$$

with $\gamma = (2-\tau)z$. Comparison of (4.3) with $c_k/c_1 = \nu_k \sim k^{-\tau}\psi(kt^{-z})$ shows that $c_1 \sim t^{-\gamma}$ ($t\to\infty$). The time dependence of the LHS of (2.6) for large k and large t can be estimated using (4.3) with $\psi(x)$ given in (A1.5), where two cases have to be distinguished.

In case (a): $1+\lambda-m < \tau < 1+\lambda$, where $m = \min(\mu', 1)$ we deduce from (A1.5*a*) that $\psi'(x) \sim I(\tau)x^{\lambda-\tau}$ with $I(\tau)$ defined in (A1.7). The result is

$$(1/c_1)\dot{\nu}_k \sim t^{\gamma-z-1}k^{1-\tau}\psi'(kt^{-z}) \sim k^{1+\lambda-2\tau}I(\tau) \tag{4.4}$$

where the relations $\gamma = z(2-\tau)$ and $z = 1/(1-\lambda)$ have been used. Thus, the LHS of (2.6) approaches a time-independent non-vanishing constant, so that the additional assumption (2.7) is violated and the *recursion relation (2.3) is not valid.*

If one makes the *ad hoc* assumption, that the LHS of (2.6) vanishes, one imposes according to (4.4) the condition

$$I(\tau)=0 \tag{4.5}$$

where $I(\tau)$ is defined in (A1.7). The solution of this transcendental equation, which we indicate by τ_R, does not seem to have any relationship to the τ exponent, which follows from Smoluchowski's equation to be $\tau = 2 - p_\lambda / w$ (see (A1.4)). The possibility that $\tau = 2 - p_\lambda / w$ equals τ_R for general class II kernels belonging to case (a): $1+\lambda - m < \tau < 1+\lambda$, can be excluded by counter examples, as will be shown in the next section.

In appendix 3 we have analysed the large-k solution of the recursion relation (2.3), $R(b_k)=0$, for class II kernels, and we have shown that its asymptotic solution $b_k \sim k^{-\tau_R}$ is also determined by the transcendental equation (4.5), as it should. It only shows that our results are internally consistent.

In case (b), where $\tau < 1+\lambda - m$, one sees that $\psi'(x) \sim x^{m-1}$, implying that the LHS of (2.6) diverges as $t \to \infty$, i.e.

$$(1/c_1)\dot{\nu}_k \sim k^m b_k s^{1+\lambda-m-\tau} \to \infty \qquad t \to \infty. \tag{4.6}$$

Thus, assumption (2.7) is violated, and the *long time behaviour of $\nu_k(t)$ is not described by the recursion (2.3)*. In case (b) the possibility of a vanishing prefactor is *a priori* excluded by the results in (A1.7). An example of a case (b) kernel with a well defined exponent $\tau = 2 - p_\lambda / w$ will be shown in the next section.

In our calculation of the LHS of (2.6) for class II kernels we have taken into account the scaling function without possible corrections to scaling, e.g. $c_k(t) \sim k^{-\tau}\psi(kt^{-z}) + k^{-\tau'}\psi_1(kt^{-z}) + \ldots$ with $\tau' > \tau$. One readily convinces oneself that such extra terms to the RHS of (4.4) are at most of relative order $k^{\tau-\tau'} \to 0$ as $k \to \infty$, and do not affect the conclusions of this section.

5. Comparison of τ and τ_R

This section deals exclusively with special examples of class II kernels. We shall compare the exponents $\tau = 2 - p_\lambda / w$, obtained from Smoluchowski's equation (1.1) using the scaling function method, with the exponent τ_R, obtained from the recursion relation (2.3). We show that the two exponents are different in general.

Without actually solving the integral equation for the scaling function $\varphi(x)$ and calculating $p_\lambda = \int \mathrm{d}x\, x^\lambda \varphi(x)$ we can determine upper and lower bounds on τ, and compare these with τ_R.

In this manner van Dongen and Ernst (1985b) have already shown for the sum kernel, $K(i,j) = i^\lambda + j^\lambda\,(0<\lambda<1)$, that the exponent $\tau_R = 1 + \frac{1}{2}\lambda$, as obtained by Leyvraz from the recursion relation, differs from the actual τ exponent, $\tau = 2 - p_\lambda / w$, at least for $\lambda < \lambda_0 \simeq 0.366$.

As a second example of a class II kernel we consider $K(i,j) = (i+j)^\lambda$ with $\lambda < 1$. An upper and lower bound on τ can be derived as follows. Consider the inequalities for $\lambda < 1$ and x, y positive

$$2^\lambda(2-2^\lambda)(xy)^\lambda(x+y)^{-\lambda} \leqslant x^\lambda + y^\lambda - (x+y)^\lambda < (xy)^\lambda (x+y)^{-\lambda}. \tag{5.1}$$

These inequalities are applied to (A1.2) with $\alpha = \lambda$ for the kernel under consideration and yield:

$$2^{\lambda-1}(2-2^\lambda)p_\lambda^2 < (1-\lambda)p_\lambda w < \tfrac{1}{2}p_\lambda^2. \tag{5.2}$$

When applied to $\tau = 2 - p_\lambda / w$, we obtain the following bounds for all $\lambda < 1$:

$$\tau_- < \tau < \tau_+ \tag{5.3a}$$

with

$$\tau_- = 2 - 2^{1-\lambda}(1-\lambda)/(2-2^\lambda) \qquad \tau_+ = 2\lambda. \tag{5.3b}$$

The lower bound reduces to $\tau_- \simeq 2\lambda - 2\lambda^2(\log 2)^2$ as $\lambda \to 0$, and (5.3) shows that $\tau \simeq 2\lambda + O(\lambda^2)$ as $\lambda \to 0$, which approaches the result $\tau = 0$ for the constant kernel $K(i,j) = 1$.

One can obtain a better upper bound on τ for $\lambda \geqslant 0.7$ using the inequality valid for $\lambda > \frac{1}{2}$ (for $\lambda < \frac{1}{2}$ the inequality is reversed):

$$(x+y)^{2\lambda} - x^{2\lambda} - y^{2\lambda} < (2^{2\lambda} - 2)(xy)^\lambda \tag{5.4}$$

yielding for all $\lambda \leqslant 1$

$$\tau < \tau'_+ = 2 - (2\lambda - 1)(2^{2\lambda} - 2). \tag{5.5}$$

Table 1 shows that one can obtain fairly good estimates for the τ exponent without actually calculating the scaling function.

Table 1. Upper and lower bounds on the τ exponent (equation (A1.4)) compared to the τ_R exponent from the recursion relation for $K(i,j) = (i+j)^\lambda$ $(0 \leqslant \lambda \leqslant 1)$. Above the dotted line τ_R exceeds the best upper bound on τ.

λ	τ_-	$\min\{\tau_+, \tau'_+\}$	τ_R
0.0+	0.00	0.00	0.00
0.1	0.19	0.20	0.25
0.2	0.36	0.40	0.44
0.3	0.52	0.60	0.61
0.4	0.66	0.80	0.77
0.5	0.79	1.00	0.91
0.6	0.91	1.20	1.04
0.7	1.02	1.37	1.17
0.8	1.11	1.42	1.29
0.9	1.20	1.46	1.40
1.0	1.28	1.50	1.50

Next, we turn to a discussion of the recursion relation. The upper bound $\tau_+ = 2\lambda$, also shows that $K(i,j) = (i+j)^\lambda$ with $\lambda < 0$ corresponds to case (b), namely $\tau < 1 + \lambda - \min(\mu', 1) = \lambda$, discussed above (4.6). This is so, since $\mu' = \infty$ according to its definition (1.4). Hence, the LHS of (2.6) diverges, and so does the infinite sum occurring in the recursion relation (2.3). Thus, for $\lambda < 0$, the recursion relation does not exist.

The kernels $K(i,j) = (i+j)^\lambda$ with $\lambda > 0$ belong to case (a), since $\lambda < \tau < 1 + \lambda$. In this τ interval the asymptotic solution of the recursion relation is given by (4.5) as the root of the transcendental equation, $I(\tau) = 0$, where $I(\tau)$ can be calculated from (A1.7), and yields

$$I(\tau) = B(1-\tau, \tau - 1 - \lambda) - \tfrac{1}{2}B(1-\tau, 1-\tau) = 0. \tag{5.6}$$

We note that $\tau_R = 1$ is in general not a solution of this equation. This can be seen by inserting $\tau = 1+\varepsilon$ ($\varepsilon \to 0$) into (5.6). The terms of $O(\varepsilon^0)$ only cancel if $\gamma+\psi(-\lambda)=0$, i.e. if $\lambda=\lambda_0 \simeq 0.567\ldots$, where γ is Euler's constant and $\psi(x)=\Gamma'(x)/\Gamma(x)$. The solution τ_R of (5.6) may be determined graphically. There exists only one solution in $(\lambda, 1+\lambda)$ which is increasing monotonically with λ and having the limiting behaviour

$$\begin{aligned} \tau_R &\simeq \tfrac{1}{2}+\lambda \qquad && \lambda \uparrow 1 \\ \tau_R &\simeq 3\lambda && \lambda \downarrow 0. \end{aligned} \tag{5.7}$$

Comparison with (5.3*a*, *b*) shows that $\tau < \tau_+ \leqslant \tau_R$ provided $\tau_R \geqslant 2\lambda$. It follows from (5.6) that $\tau_R = \tau_+ = 2\lambda$ for $\lambda = \frac{1}{3}$ only. Thus, we have shown that $\tau < \tau_R$ for all $\lambda \leqslant \frac{1}{3}$. A more detailed comparison is given in table 1.

With the two classes of counter examples of this section we have shown that the solution of the recursion relation (2.3) has in general no relevance for the long time behaviour of the size distribution in class II systems.

6. Conclusion

The most important and new results of this paper have already been extensively described in the introduction. Here we only summarise the most important conclusion. In gelling and non-gelling systems of class I, defined through (1.3) with $\mu > 0$, the cluster size distribution approaches for long times to the exact solution Cb_k/t ($k = 1, 2, \ldots$) or $c_k(t)/c_1(t) \to b_k$ ($k = 1, 2, \ldots$), where the b_k's are independent of $c_k(0)$ and determined by the recursion relation (2.3), $R(b_k)=0$ with $b_1 = 1$.

The results obtained both in the scaling function method, and in the recursion relation method, have to some extent the status of a conjecture, since the major arguments presented are only based on self-consistency, and cannot rule out completely different asymptotic behaviour. However, for the exactly solved models in class I and II our predictions are confirmed in full detail, as will be shown below. In class III no exactly solved models are available.

It is worthwhile to stress that class I systems (gelling and non-gelling) show a more universal long time behaviour than class II systems. We illustrate this through three exactly solved models.

In gelling class I models, $K(i,j)=ij$ ($\lambda = 2$, $\mu = 1$), we have already seen in § 3.2 that $c_k(t)/c_1(t) \simeq b_k(1+O(t^{-2}))$ as $t \to \infty$ for $k = 1, 2, \ldots$ with $b_k = k^{k-2}e^{1-k}/k!$, independent of $c_k(0)$. Unfortunately, non-gelling models of class I, that can be solved for general $c_k(0)$, are not available.

Next we consider the class II models $K(i,j)=i+j$ ($\lambda = 1$, $\mu = 0$) and $K(i,j)=1$ ($\lambda = 0$, $\mu = 0$), that have been solved for general initial distributions. For the sum kernel we have already shown in (4.2) that $c_k(t)/c_1(t)$ for $k = 2, 3, \ldots$ approaches a non-universal constant depending on the initial distribution. However, in the scaling limit the size distribution approaches for general initial distributions a universal scaling function, namely $c_k(t) \simeq (s(t))^{-2}\varphi(k/s(t))$ for $k \to \infty$, $s(t) \to \infty$ and $k/s(t) = \text{constant}$, where $\varphi(x) = (2\pi)^{-1/2}x^{-3/2}\exp(-x/2)$. The expression for $\varphi(x)$ can be derived from the exact solution (Ziff *et al* 1984), where the mean cluster size is given by $s(t) = M_2(t)/M_1(t) = M_2(0)\,e^{2t}$ with $M_n(t) = \Sigma\, k^n c_k(t)$.

For the constant kernel $K(i,j)=1$ one easily shows that $c_k(t)/c_1(t)$ approaches a constant, depending on $c_k(0)$, whereas in the scaling limit $k \to \infty$, $s(t) \sim t \to \infty$ with $kt^{-1} = \text{fixed}$, the size distribution approaches $c_k(t) \simeq s^{-2}\varphi(k/s)$ where $\varphi(x) = e^{-x}$.

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Appendix 1

This appendix contains a short summary of results from the scaling function method obtained by van Dongen and Ernst (1985a), relevant for non-gelling models.

In non-gelling models ($\lambda < 1$) the size distribution approaches for large k and large t the scaling form

$$c_k(t) \simeq s^{-2}\varphi(k/s). \tag{A1.1}$$

Using Smoluchowski's equation, we can derive an integral equation for the scaling function $\varphi(x)$. By separating the x and t dependence, it follows that $\dot{s}s^{-\lambda} = w$ or $s(t) \sim t^z$ ($t \to \infty$; $z = 1/(1-\lambda)$), where w is a separation constant. Furthermore, the moment equations of the $\varphi(x)$ equation yield:

$$(1-\alpha)p_\alpha w = \tfrac{1}{2}\int_0^\infty \mathrm{d}x \int_0^\infty \mathrm{d}y\, K(x,y)\varphi(x)\varphi(y)[x^\alpha + y^\alpha - (x+y)^\alpha] \tag{A1.2}$$

where the αth moment is defined as

$$p_\alpha = \int_0^\infty \mathrm{d}x\, x^\alpha \varphi(x). \tag{A1.3}$$

From the integral equation one shows that $\varphi(x)$ decays exponentially at large x. At small x, $\varphi(x) \simeq Bx^{-\tau}$ ($x \to 0$) in class I and II systems, whereas in class III systems $\varphi(x) \sim \exp(-x^{-|\mu|})(x \to 0)$.

In the non-gelling class I models ($\mu > 0$, $\lambda < 1$), the τ exponent is given by $\tau = 1 + \lambda$. In class II systems ($\mu = 0$) the τ exponent is given by

$$\tau = 2 - p_\lambda / w \tag{A1.4}$$

and depends through the moment p_λ on the explicit form of the (unknown) $\varphi(x)$, and satisfies $\tau < 1 + \lambda$. To proceed we have to distinguish two cases: (a) $1 + \lambda - m < \tau < 1 + \lambda$, and (b) $\tau < 1 + \lambda - m$, where $m \equiv \min(\mu', 1)$ with μ' defined by (1.4). The corresponding small-x behaviour is

$$\varphi(x) = Bx^{-\tau}\psi(x) \simeq \begin{cases} Bx^{-\tau}(1 + bx^{1+\lambda-\tau} + \dots) & \text{case a} \\ Bx^{-\tau}(1 + bx^m + \dots) & \text{case b} \end{cases} \tag{A1.5}$$

where

$$b = \begin{cases} BI(\tau)/[(1+\lambda-\tau)w] & \text{case a} \\ K_1 p_{\lambda-\mu'}/[\mu' w] & \text{case b, } \mu' < 1 \\ \lambda p_{\lambda-1}/w & \text{case b, } \mu' > 1 \end{cases} \tag{A1.6}$$

with K_1 is defined in (1.4) and

$$I(\tau) = \lim_{\varepsilon \downarrow 0}\left(\int_\varepsilon^\infty \mathrm{d}x[K(1,x) - x^\lambda]x^{-\tau} - \tfrac{1}{2}\int_\varepsilon^{1-\varepsilon} \mathrm{d}x\, K(x, 1-x)[x(1-x)]^{-\tau}\right). \tag{A1.7}$$

Appendix 2

In this appendix we discuss, as an example, the complications arising in class I ($\mu > 0$) models if dimers, instead of monomers, are least reactive, i.e. if $K(2,j) < K(k,j)$ ($k \neq 2, j = 1, 2, \ldots$). In this case it is intuitively clear that dimers are the rate-determining species, and the obvious ansatz is

$$c_k(t)/c_2(t) \to b_k \qquad t \to \infty \tag{A2.1}$$

where the b_k are finite, non-negative constants.

First we show that $b_1 = 0$. In order to obtain a contradiction, assume that $b_1 > 0$, i.e. that $c_1(t) \sim c_2(t)$. In this case we may copy the discussion of § 3, and (3.4) implies $c_2(t)/c_1(t) \sim t^{\alpha(2)} \to \infty$ ($t \to \infty$), with $\alpha(2) = 1 - E_2/E_1$, in contradiction with our assumption $b_1 > 0$. We conclude that $b_1 = 0$. In order to calculate the asymptotic time dependence of $c_2(t)$, we define again

$$E_k \equiv \sum_{j=1}^{\infty} K(k,j) b_j \tag{A2.2}$$

and approximate (1.1) for $k = 2$ as follows

$$\dot{c}_2 = \tfrac{1}{2}K(1,1)(c_1)^2 - c_2\sigma_2 \simeq -(c_2)^2 E_2 \qquad t \to \infty \tag{A2.3}$$

implying $c_2(t) \simeq (E_2 t)^{-1}$ ($t \to \infty$).

Knowing $c_2(t)$ ($t \to \infty$) we can calculate $c_k(t)$ for general k. Consider, first the case $k = 1$:

$$\dot{c}_1 = -c_1\sigma_1 \simeq -c_1(E_1/E_2 t) \qquad t \to \infty. \tag{A2.4}$$

It follows that $c_1(t) \sim t^{-\beta(1)}(t \to \infty)$, with $\beta(1) = E_1/E_2$. In general, we define $\beta(k)$ by

$$c_k(t) \sim t^{-\beta(k)} \qquad t \to \infty. \tag{A2.5}$$

The exponent $\beta(k)$ is determined by a simple recursion relation. To see this, consider (3.4), where now $S_k(t) \simeq (E_k/E_2)\log t$ ($t \to \infty$). If the integral in (3.4) converges, i.e. if $E_k/E_2 < (\beta(i) + \beta(j) - 1)$ for all i, j with $i + j = k$, then one finds $c_k(t) \sim \exp(-S_k(t)) \sim t^{-\beta(k)}$, with $\beta(k) = E_k/E_2$. Alternatively, if the integral in (3.4) diverges, then $\beta(k) = \min\{\beta(i) + \beta(j) - 1\}$, with $i + j = k$. These results may be combined into a single recursion relation for $\beta(k)$, namely

$$\beta(k) = \min_{i+j=k}\{E_k/E_2, \beta(i) + \beta(j) - 1\};\ \beta(1) = E_1/E_2. \tag{A2.6}$$

This recursion relation shows that $\beta(k) = 1$ if k is even, and $\beta(k) > 1$ if k is odd. This implies $b_k > 0$ for even values of k and $b_k = 0$ for odd k values.

The factors b_k, which determine the E_k and, hence, the exponents $\beta(k)$, may be calculated from a recursion relation. In an analogous fashion to the procedure in § 3 one finds instead of (2.3):

$$\tfrac{1}{2}\sum_{i+j=k} K(i,j) b_i b_j = b_k \sum_{j=1}^{\infty} (K(k,j) - K(2,j)) b_j \tag{A2.7}$$

which is to be solved subject to the initial condition $b_1 = 0$, $b_2 = 1$.

Contained in the class of systems where dimers are least reactive, are systems without monomers, i.e. $c_1(0) = 0$, but $c_2(0) \neq 0$ and possibly $K(1,j) < K(2,j)$. In this case the initial condition of (A2.6) is $\beta(1) = \infty$.

The example discussed in this section, where dimers are least reactive, may be generalised to a situation where l-mers are the least reactive species. In this case one finds that $c_k(t)/c_l(t) \to b_k$ $(t \to \infty)$, where b_k is the solution of:

$$\tfrac{1}{2} \sum_{i+j=k} K(i,j) b_i b_j = b_k \sum_{j=1}^{\infty} (K(k,j) - K(l,j)) b_j \tag{A2.8}$$

to be solved with initial condition $b_l = 1$, $b_j = 0 (j < l)$. The k-mer concentration behaves asymptotically as $c_k(t) \sim t^{-\beta(k)}$, where $\beta(k)$ is the solution of (A2.6) with E_2 replaced by E_l. The special case where $c_l \neq 0$, but $c_j(0) = 0$ $(j < l)$ leads to the same results, now with $\beta(1) = \ldots = \beta(l-1) = \infty$.

Appendix 3

In this appendix we restrict ourselves to class II kernels and analyse the asymptotic solution of the recursion relation, $R(b_k) = 0$, given in (2.5). We are in particular interested in the large-k solutions of the general form $b_k \simeq Bk^{-\tau}$ $(k \to \infty)$. To admit such solutions, the infinite sum in (2.3) must exist, which imposes the following requirement on τ:

$$\tau > \max\{\lambda,\ 1 + \lambda - \mu'\} \equiv 1 + \lambda - m \tag{A3.1}$$

as can be deduced from (1.4). Physically acceptable solutions b_k $(k = 1, 2, \ldots)$ of the recursion relation must be non-negative; therefore the infinite sum in (2.3) must be non-negative. This requirement immediately shows that the recursion relation method cannot be valid for those class II kernels with $K(k,j) - K(1,j) \leq 0$ for $k = 1, 2, \ldots$. Examples of such kernels can, in fact, simply be constructed if the degree of homogeneity $\lambda \leq 0$, e.g. $K(i,j) = 1$ or $K(i,j) = (i+j)^\lambda$ $(\lambda \leq 0)$.

In the remainder of this section we assume that $K(i,j)$ is such that the infinite sum in (2.3) is bounded and positive for all $k > 1$.

The result $\tau = 1 + \lambda$, obtained in (3.12) for the non-gelling models of class I, does not lead to a consistent large-k solution of (2.3), because the infinite sum E_1 and the integral occurring in (3.12) are both divergent for $\tau = 1 + \lambda$. The assumption $\tau > 1 + \lambda$ leads to a contradiction, since it implies $\tau = 1 + \lambda$ on account of (3.12). These results, in combination with (A3.1), set the following bounds on the range of possible values of τ:

$$1 + \lambda - m < \tau < 1 + \lambda. \tag{A3.2}$$

In this τ interval, the infinite sum in (2.3) is convergent, whereas the individual terms E_k and E_1 are divergent.

To determine asymptotic solutions of the recursion relation in class II, we insert the ansatz $b_k \simeq Bk^{-\tau}$ $(k > k_0)$ into (2.3) and test for self-consistency. Denoting the first and second term in $R(b_k)$ by R_1 and R_2 respectively, we find from (1.2), (1.3) and (1.4):

$$R_1 \simeq Bk^{\lambda-\tau} \sum_{j=1}^{k_0} b_j + B^2 k^{1+\lambda-2\tau} \int_{k_0/k}^{1/2} \mathrm{d}x\, K(x, 1-x)[x(1-x)]^{-\tau} \tag{A3.3}$$

and

$$R_2 \simeq -Bk^{\lambda-\tau} \sum_{j=1}^{k_0} b_j + Bk^{-\tau} \sum_{j=1}^{k_0} K(1,j) b_j - B^2 k^{1+\lambda-2\tau} \int_{k_0/k}^{\infty} \mathrm{d}x\, [K(1,x) - x^\lambda]. \tag{A3.4}$$

We note that the first terms in R_1 and R_2 cancel. Since we assume that τ is inside the interval (A3.2), the integral $\int^{\infty} \mathrm{d}x\,(\ldots)$ in (A3.4) converges, and combination of the remaining terms in (A3.3) and (A3.4) yields for the recursion relation (2.3) as $k \to \infty$:

$$Bk^{-\tau} \sum_{j=1}^{k_0} K(1,j) b_j \simeq B^2 k^{1+\lambda-2\tau} I(\tau) \tag{A3.5}$$

where $I(\tau)$ is defined in (A1.7). The coefficient $I(\tau)$ is only well defined if τ is sufficiently small, so that the integral in (A1.7) converges at the lower limit. This imposes the requirement $\tau < 2 + \mu'$, since the small x divergences cancel. This requirement is automatically fulfilled. Thus the RHS of (A3.5) dominates over the LHS, and (A3.5) can only lead to a consistent solution if the coefficient $I(\tau)$ vanishes, i.e. if the transcendental equation

$$I(\tau) = 0 \tag{A3.6}$$

has a solution $\tau = \tau_R$ in the interval (A3.2). Thus, we have found the asymptotic solution of the recursion relation, $R(b_k) = 0$, to be $b_k \sim k^{-\tau_R}$ $(k \to \infty)$, and we note that (A3.6) is identical to (4.5), which was the condition that the LHS of (2.6) vanishes in case (a), i.e. for τ values satisfying (A3.2).

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