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Scaling Solutions of Smoluchowski's Coagulation Equation

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We investigate the structure of scaling solutions of Smoluchowski's coagulation equation, of the form $c_k(t) \sim s(t)^{-\tau} \varphi(k/s(t))$, where $c_k(t)$ is the concentration of clusters of size k at time t, $s(t)$ is the average cluster size, and $\varphi(x)$ is a scaling function. For the rate constant $K(i, j)$ in Smoluchowski's equation, we make the very general assumption that $K(i, j)$ is a homogeneous function of the cluster sizes i and j: $K(i, j) = a^{-\lambda} K(ai, aj)$ for all $a > 0$, but we restrict ourselves to kernels satisfying $K(i, j)/j \to 0$ as $j \to \infty$. We show that gelation occurs if $\lambda > 1$, and does not occur if $\lambda \leqslant 1$. For all gelling and nongelling models, we calculate the time dependence of $s(t)$, and we derive an equation for $\varphi(x)$. We present a detailed analysis of the behavior of $\varphi(x)$ at large and small values of x. For all models, we find exponential large-x behavior: $\varphi(x) \sim Ax^{-\lambda} e^{-\delta x}$ as $x \to \infty$ and, for different kernels $K(i, j)$, algebraic or exponential small-x behavior: $\varphi(x) \sim Bx^{-\tau}$ or $\varphi(x) = \exp(-Cx^{-|\mu|} + \cdots)$ as $x \downarrow 0$.

KEY WORDS: Kinetics of clustering; irreversible aggregation; scaling laws for cluster size distribution; similarity solutions; self-preserving mass spectrum.

1. INTRODUCTION

In this paper we study the universal (scaling) properties of the solutions of Smoluchowski's coagulation equation. A summary of the results presented here has been published elsewhere.[1]

We recall that Smoluchowski's coagulation equation is a mathematical model describing irreversible aggregation processes, which consists of an

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infinite set of chemical rate equations for the concentrations $c_k(t)$ of clusters of size k ($k = 1, 2, \ldots$), or k-mers:

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

Here $K(i, j)$ is the rate constant for the combination of an i- and a j-mer. Possible breakup of clusters is not taken into account. For a review on Smoluchowski's equation we refer to the literature.[2,3]

Many authors have noted[4–13] for various special choices of the rate constants $K(i, j)$ that the cluster size distribution $c_k(t)$ approaches a scale-invariant form in the scaling limit (S), where the mean cluster size $s(t)$ diverges: $s(t) \to \infty$, and $k \to \infty$, with the scaling argument $x \equiv k/s(t)$ kept fixed:

$$c_k(t) \xrightarrow{\text{S}} s(t)^{-\tau'} \varphi(k/s(t)) \tag{1.2}$$

Thus, in the scaling limit, $c_k(t)$ becomes independent of the details of the initial distribution. In this paper we calculate the time dependence of the mean cluster size $s(t)$, and we study the shape of the scaling function $\varphi(x)$ for different classes of coagulation rates $K(i, j)$.

Since most kernels $K(i, j)$ used in the literature (see, e.g., Ref. 3) are homogeneous functions of their arguments, at least for large cluster sizes i and j, we restrict ourselves to such kernels, and characterize $K(i, j)$ by the exponents μ and ν, which describe its i and j dependence if $j \gg i$ (or $i \gg j$):

$$K(ai, aj) = a^{\lambda} K(i, j) = a^{\lambda} K(j, i) \tag{1.3a}$$

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

We distinguish kernels with $\mu > 0$ (class I), $\mu = 0$ (class II), and $\mu < 0$ (class III). Moreover, we impose the physical restriction $\nu \leqslant 1$, since the reaction rate j^{ν} of a large j-mer (i.e., $j \gg i$) should not increase faster than its volume, and similarly $\lambda \leqslant 2$, since for clusters of equal size, $K(j, j) = j^{\lambda} K(1, 1)$ should not increase faster than j^2.

Furthermore, within the class of homogeneous kernels (1.3), we distinguish *nongelling* models, where the mean cluster size $s(t)$ remains finite for all times $t < \infty$, and *gelling* models, where a gelation transition, characterized by a divergence of $s(t)$, occurs at a finite time t_c, the *gelpoint*. Thus, scaling behavior, which is observed as $s(t) \to \infty$, refers to nongelling systems at large times ($t \to \infty$), or to gelling systems in the limit $t \to t_c$. Which systems gel and which systems do not will be the subject of Section 2.

The existence of scaling solutions of Smoluchowski's equation may be seen as follows. Since the scaling limit refers to large clusters containing many monomeric units, it is appropriate to treat the cluster size k as a continuous variable. The continuous analog of Eq. (1.1) is

$$\frac{\partial c}{\partial t}(k, t) = \frac{1}{2}\int_0^k dl\, K(l, k-l)\, c(l, t)\, c(k-l, t) - c(k, t)\int_0^\infty dl\, K(k, l)\, c(l, t) \tag{1.4}$$

Substitution of the scaling Ansatz (1.2) into Eq. (1.4) shows that Smoluchowski's equation admits exact solutions of scaling or similarity form, satisfying

$$-w(\tau'\varphi(x) + x\varphi'(x)) = \frac{1}{2}\int_0^x dy\, K(y, x-y)\, \varphi(y)\, \varphi(x-y) - \varphi(x)\int_0^\infty dy\, K(x, y)\, \varphi(y) \tag{1.5a}$$

$$\dot{s} = ws^{\lambda+2-\tau'} \tag{1.5b}$$

Here w is a separation constant for the x and t dependence. A more careful derivation of the scaling equations (1.5a), (1.5b) will be given in Section 3. We remark that the reason Smoluchowski's equation (1.5) admits similarity solutions is that (1.5) is invariant under a semigroup of similarity transformations (see, e.g., Ref. 8).

This paper is organized as follows. In Section 2 we classify the rate constants corresponding to gelling or nongelling systems. In Section 3 we derive equations for the mean cluster size $s(t)$ and for the scaling function $\varphi(x)$. The structure of $\varphi(x)$ is studied in Section 4 for nongelling models and in Section 5 for gelling models. Section 6 is devoted to a special class of nongelling systems, not considered in Section 4. Finally, we summarize and discuss our results in Section 7. Certain technical details are given in Appendices A and B.

2. CLASSIFICATION OF GELLING AND NONGELLING MODELS

The gelation transition, which occurs in gelling systems at the gelpoint, is characterized by a divergence of the mean cluster size $s(t)$, and by the onset of a mass flow from the finite-size clusters (sol) to clusters of infinite size (gel). Here, we determine which coagulation kernels allow for such a mass flow, and we study the structure of postgel solutions, i.e.,

solutions of Eq. (1.1) for $t < t_c$. The arguments presented in this section are the generalization to homogeneous kernels of certain results in Refs. 7 and 8. In these references one considers the product kernel $K_{ij} = i^{\omega} j^{\omega}$ (with $\omega \leqslant 1$), which is contained in (1.3a), (1.3b) as a special case.

In order to study the possibility of gelling solutions, we consider the mass flow

$$-\dot{M}^{(k)}(t) = -\sum_{j=1}^{k} j\dot{c}_j$$

from the clusters of size $j \leqslant k$ to the clusters of size $j > k$:

$$-\dot{M}^{(k)}(t) = -\sum_{j=1}^{k} j\dot{c}_j = \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} iK(i, j)\, c_i c_j \tag{2.1}$$

Equation (2.1) is equivalent to Eq. (1.1), and may be derived by multiplying both sides of (1.1) with k, summing over k from 1 to l, and relabeling the indices $k \to j$ and $l \to k$. Equation (2.1) shows that if $c_k(t)$ vanishes sufficiently rapidly as $k \to \infty$, then

$$\dot{M}^{(\infty)}(t) = \lim_{k \to \infty} \dot{M}^{(k)}(t) = 0$$

and one finds that $M_1(t)$, the total mass contained in finite-size clusters (sol mass), is constant:

$$M_1(t) = \sum_{k=1}^{\infty} kc_k(t) = \text{const} = 1 \tag{2.2}$$

The constant in (2.2) may be set equal to unity by an appropriate choice of the unit of volume. Equation (2.2) applies to nongelling systems, and to gelling systems if $t < t_c$. In these cases $c_k(t)$ decays exponentially rapidly as a function of k.[14,15]

Gelling solutions, for which the mass flow

$$\dot{M}^{(\infty)}(t) = \lim_{k \to \infty} \dot{M}^{(k)}(t)$$

is finite and nonvanishing, are possible only if $c_k(t)$ decays sufficiently slowly (algebraically) as a function of k:

$$c_k(t) \sim B(t)\, k^{-\tau} \qquad (k \to \infty) \tag{2.3}$$

Substitution of the Ansatz (2.3) into Eq. (2.1) shows that for $k \to \infty$:

$$-\dot{M}^{(\infty)}(t) \sim [B(t)]^2\, k^{3+\lambda-2\tau} J(\tau) \qquad (k \to \infty) \tag{2.4a}$$

Here $J(\tau)$ is defined as

$$J(\tau) = \int_0^1 dx \int_{1-x}^{\infty} dy\, xK(x, y)(xy)^{-\tau} \tag{2.4b}$$

and depends on the parameter τ. The lhs of Eq. (2.4a) can only be finite and nonvanishing for all times past the gelpoint if the rhs is independent of k as $k \to \infty$, i.e., if

$$\tau = (\lambda + 3)/2 \tag{2.5a}$$

The possibility of divergence of the rhs of Eq. (2.4a) is physically only acceptable at *one* instant of time, the gelpoint. Since we are looking for solutions for all $t > t_c$, $|\dot{M}^{(\infty)}(t)|$ must be finite, and so is the rhs of (2.4a). It follows from (2.4a) that the prefactor $B(t)$ is related to the mass flow $-\dot{M}_1(t)$ as

$$B(t) = [-\dot{M}_1(t)/J(\tau)]^{1/2} \qquad (t \geqslant t_c) \tag{2.5b}$$

Thus, for $t \geqslant t_c$ the conservation law (2.2) is replaced by

$$M_1(t) + G(t) = 1 \tag{2.6}$$

where $M_1(t)$ and $G(t)$ are respectively the sol and gel mass fractions.

Equation (2.3) with (2.5) is an acceptable solution provided certain consistency requirements are satisfied. The first requirement is that the sol mass $M_1(t) = \sum_{k=1}^{\infty} kc_k(t)$ should be finite for $t > t_c$, implying $\tau > 2$, or $\lambda > 1$ due to (2.5a). Second, the convergence of the integral (2.4b) imposes the restriction

$$1 + \nu < \tau < 2 + \mu \tag{2.7}$$

For $\lambda > 1$, $\nu \leqslant 1$, and τ as in (2.5a), the condition (2.7) is always met. This shows the occurrence (or absence) of a gelation transition for homogeneous kernels (1.3) with $\lambda > 1$ (or $\lambda \leqslant 1$).

How to determine the value of the pre-gel exponent τ' in (1.2) for gelling models? We start from the scaling form (1.2) in gelling systems, and we impose two requirements. First, we require that at the gelpoint $c_k(t_c)$ is finite and nonvanishing. This can only happen if, for small x, $\varphi(x) \sim Bx^{-\alpha}$ with $\alpha = \tau'$, since in this case

$$\lim_{t \uparrow t_c} c_k(t) \sim s^{-\tau'} B(k/s)^{-\alpha} \sim Bk^{-\tau'} \qquad (k \gg 1) \tag{2.8}$$

Second we assume that for large k the prediction (2.3) from the postgel

solution is also valid *at* the gelpoint t_c. Combination of (2.3), (2.5), and (2.8) then gives the desired value of the exponent τ':

$$\tau' = \tau = (\lambda + 3)/2 \tag{2.9}$$

In addition we find that the mass flux at the gelpoint is related to the prefactor B in the scaling function: $\dot{M}(t_c) = -B^2 J(\tau)$. We remark that the arguments leading to Eqs. (2.8) and (2.9) are *not* rigorous. The reason is that pre- and postgel results (1.2) and (2.3) are valid in the scaling limit and in the limit $k \to \infty$, respectively. They need not be valid in the limit $t \to t_c$, with $k \gg 1$ fixed, where they are applied.

Next we discuss nongelling models. It has been proved by White[16] that a gelation transition does not occur if the reaction rate $K(i, j)$ can be bounded from above by $(i + j)$. Thus, gelation does not occur for any model with $\lambda \leqslant 1$, since in this case there exists some constant $C < \infty$ such that

$$K(i, j) \leqslant C(i + j) \tag{2.10}$$

For kernels in classes I and II ($\mu \geqslant 0$) this is obvious, since $K(i, j) = (i + j)^{\lambda} K(y, 1 - y)$, with $y \equiv i/(i + j)$, and $K(y, 1 - y)$ is bounded for all $y \in [0, 1]$. In class III ($\mu < 0$), the kernel $K(i, j)$ can be bounded by $(i^{\nu} + j^{\nu})$ due to (1.3b). This in turn implies (2.10). In summary: the occurrence of a gelation transition is determined only by the degree of homogeneity λ of the coagulation kernel $K(i, j)$: gelation occurs if $\lambda > 1$; it is absent for $\lambda \leqslant 1$.

The value of the exponent τ' in nongelling systems ($\lambda \leqslant 1$) is determined by the normalization (2.2) of the sol mass. Substitution of the scaling form (1.2) into Eq. (2.2) shows that (2.2) imposes

$$1 = M_1(t) \sim s^{2-\tau'} \int_0^{\infty} dx\, x\varphi(x) \qquad [s(t) \to \infty] \tag{2.11}$$

Thus, necessarily,

$$\tau' = 2 \tag{2.12}$$

As a consequence, the first moment of the scaling function is normalized to unity, $p_1 = 1$, where in general the moments p_α of $\varphi(x)$ are defined by

$$p_\alpha = \int_0^{\infty} dx\, x^{\alpha} \varphi(x) \tag{2.13}$$

In the derivation of (2.12) it has been assumed *that all mass is contained in the scaling regime*, i.e., that the integral p_1 converges. Thus, for nongelling

systems the condition $p_1 < \infty$ serves as a consistency requirement on possible scaling solutions $\varphi(x)$. *For gelling systems*, where for small x, $\varphi(x)$ is given by $\varphi(x) \sim Bx^{-\tau}$, with $\tau > 2$, *this condition is certainly not fulfilled.* In this case the mass contained in the scaling region $k/s(t) \geqslant \varepsilon$ (with $\varepsilon > 0$ fixed) vanishes as $s(t)^{2-\tau} \to 0$ as $s(t) \to \infty$.

3. DERIVATION OF AN EQUATION FOR THE SCALING FUNCTION

In Section 3.1 we derive, directly from Smoluchowski's equation (1.1), a nonlinear integrodifferential equation for the scaling function $\varphi(x)$. In our analysis it is often more convenient to use an equivalent nonlinear integral equation for $\varphi(x)$, to be derived in Section 3.2. The exponent τ', which has been defined in (1.2), is left unspecified here, so that our results are applicable for gelling and nongelling systems, where $\tau' = (\lambda + 3)/2$ and $\tau' = 2$, respectively (see Section 2).

3.1. An Integrodifferential Equation for $\varphi(x)$

To obtain an equation for the scaling function $\varphi(x)$, we insert the scaling hypothesis (1.2) into Eq. (1.1), where terms involving cluster sizes i much smaller than $k = xs(t)$, i.e., $i/k < \varepsilon \ll 1$, are treated separately:

$$
\begin{aligned}
&-[\tau'\varphi(x) + x\varphi'(x)]\, \dot{s} s^{-\tau'-1} \\
&\quad = s^{-2\tau'} \left[\frac{1}{2} \sum_{i=\varepsilon k}^{(1-\varepsilon)k} K(i, k-i)\, \varphi(i/s)\, \varphi((k-i)/s) \right. \\
&\qquad \left. - \varphi(k/s) \sum_{j=\varepsilon k}^{\infty} K(k, j)\, \varphi(j/s) \right] \\
&\qquad + s^{-\tau'} \sum_{i=1}^{\varepsilon k} [K(i, k-i)\, \varphi((k-i)/s) - K(i, k)\, \varphi(k/s)]\, c_i \qquad (3.1)
\end{aligned}
$$

For large s, the first two terms in the rhs of (3.1) may be approximated by an integral over $y = i/s(t)$ if we use the homogeneity property (1.3a) of the kernel $K(i, j)$. The last two terms in the rhs of (3.1) may be calculated with the help of (1.3b), i.e.,

$$
i^{\mu}[(k-i)^{\nu}\, \varphi((k-i)/s) - k^{\nu}\varphi(k/s)] \simeq -i^{\mu+1} s^{\nu-1} \frac{d}{dx} [x^{\nu}\varphi(x)] \qquad (3.2)
$$

Insertion of (3.2) into (3.1) shows that for large k and s, with $k/s(t)$ fixed, Eq. (3.1) reduces to

$$-(\tau'\varphi + x\varphi')\,\dot{s}s^{\tau'-\lambda-2}$$
$$= \frac{1}{2}\int_{\varepsilon x}^{(1-\varepsilon)x} dy\, K(y, x-y)\,\varphi(y)\,\varphi(x-y)$$
$$-\varphi(x)\int_{\varepsilon x}^{\infty} dy\, K(x, y)\,\varphi(y) - s^{\tau'-\mu-2}(x^{\nu}\varphi)' \sum_{i=1}^{\varepsilon k} i^{\mu+1}c_i \quad (3.3)$$

with $0 < \varepsilon \ll 1$ fixed.

As a next step, we show that for $s(t) \to \infty$, the third term in the rhs of (3.3) approaches a constant independent of t, which vanishes upon taking the limit $\varepsilon \to 0$:

$$g_{\varepsilon}(t) \equiv s^{\tau'-\mu-2} \sum_{i=1}^{\varepsilon k} i^{\mu+1}c_i \to \int_0^{\varepsilon x} dy\, y^{1+\mu}\varphi(y) \qquad (s \to \infty) \qquad (3.4)$$

To see this, we assume the opposite, namely that $g_{\varepsilon}(t)$ diverges as $s \to \infty$. This could happen if the rhs of Eq. (3.4) diverges at its lower boundary. Other possibilities, such as $g_{\varepsilon}(t) \to 0$, are excluded, since $g_{\varepsilon}(t)$ can be bounded from below as $s \to \infty$ by the contribution from i values with $\varepsilon k/2 < i \leqslant \varepsilon k$:

$$g_{\varepsilon}(t) \geqslant \int_{\varepsilon x/2}^{\varepsilon x} dy\, y^{1+\mu}\varphi(y) > 0$$

If $g_{\varepsilon}(t)$ diverges as $s \to \infty$, then Eq. (3.3) reduces to

$$(\tau'\varphi + x\varphi')\,\dot{s}s^{\tau'-\lambda-2} \sim g_{\varepsilon}(t)(x^{\nu}\varphi)' \qquad [s(t) \to \infty] \qquad (3.5a)$$

with

$$g_{\varepsilon}(t) \sim s^{\tau'-\mu-2}M_{1+\mu}(t) \qquad (3.5b)$$

In the derivation of (3.5b) we have replaced $\sum_{i=1}^{\varepsilon k} i^{\mu+1}c_i$ by

$$M_{1+\mu}(t) \equiv \sum_{i=1}^{\infty} i^{1+\mu}c_i(t)$$

This is allowed since i values with $i > \varepsilon k$ give only a constant contribution to $g_{\varepsilon}(t)$, which is negligible as $s \to \infty$.

Separation of the x and t dependence in Eq. (3.5) gives first an equation for the time dependence of the mean cluster size:

$$\dot{s} \sim ws^{\nu}M_{1+\mu} \qquad (s \to \infty) \qquad (3.6a)$$

The separation constant w in (3.6a) is positive, since the mean cluster size increases as a function of time. Second, we find an equation for the scaling function $\varphi(x)$:

$$w(\tau'\varphi + x\varphi') = (x^{\nu}\varphi)' \tag{3.6b}$$

Equation (3.6b) may readily be integrated. The result is

$$\varphi(x) = x^{-\nu} \exp\left[w(\tau' - \nu) \int_{x_0}^{x} dy/(y^{\nu} - wy) \right] \tag{3.7}$$

where x_0 is some arbitrary integration constant. The function $\varphi(x)$ in (3.7) has a singularity at the point $x_s = w^{1/(\nu-1)}$, with $\varphi(x) \to \infty$ as $x \to x_s$. Thus, $\varphi(x)$ is not acceptable as a scaling function, and we conclude that the assumption that $g_\varepsilon(t)$ diverges as $s \to \infty$ is incorrect. This implies that for large $s(t)$, $g_\varepsilon(t)$ converges to a constant, as indicated in (3.4). This constant vanishes in the limit $\varepsilon \to 0$.

Consider again Eq. (3.3). As we have seen, the third term on the right vanishes in the limit $s(t) \to \infty$, $\varepsilon \to 0$. As a consequence, the x and t dependences of (3.3) are separated, so that for some finite *constant* $w > 0$ it should hold that

$$\dot{s} s^{\tau' - \lambda - 2} = w \tag{3.8a}$$

Furthermore, we find a nonlinear integrodifferential equation for the scaling function $\varphi(x)$:

$$-w(\tau'\varphi + x\varphi') = \lim_{\varepsilon \downarrow 0} \left[\frac{1}{2} \int_{\varepsilon x}^{(1-\varepsilon)x} dy\, K(y, x-y)\, \varphi(y)\, \varphi(x-y) - \varphi(x) \int_{\varepsilon x}^{\infty} dy\, K(x, y)\, \varphi(y) \right] \tag{3.8b}$$

Equations (3.8a), (3.8b) give the main result of this subsection.

The ε limit in this equation requires some comments. If $\varphi(x)$ vanishes as $x \downarrow 0$, the limit $\varepsilon \downarrow 0$ of the separate terms does exist. We can set $\varepsilon = 0$ in Eq. (3.8b) and obtain a nonlinear integrodifferential equation for $\varphi(x)$, as already derived by Friedlander *et al.*[4-6]:

$$-w(\tau'\varphi + x\varphi') = \frac{1}{2} \int_{0}^{x} dy\, K(y, x-y)\, \varphi(y)\, \varphi(x-y) - \varphi(x) \int_{0}^{\infty} dy\, K(x, y)\, \varphi(y) \tag{3.9}$$

In cases where $\varphi(x)$ behaves algebraically as $x \downarrow 0$, we use Eq. (1.3) to analyze the small-x behavior of the terms on the rhs of (3.8b). The ε limit in the separate terms only exists if

$$\tau < 1 + \mu \tag{3.10a}$$

but for τ values in the range

$$1 + \mu < \tau < 2 + \mu \tag{3.10b}$$

the separate terms contain cancelling infinities and only the ε limit of the complete rhs of Eq. (3.8b) exists. This makes Eq. (3.8b) rather awkward for analytic and numerical analysis. In the next subsection we therefore derive a different representation of (3.8b), which is free of cancelling infinities.

Equation (3.8b) has the following invariance properties. Let $\varphi(x)$ be the solution of (3.8b) for some constant $w > 0$. Then for all $a, b > 0$,

$$\bar{\varphi}(\bar{x}) = b\varphi(\bar{x}/a) \tag{3.11a}$$

is also a solution of (3.8b), corresponding to

$$\bar{w} = ba^{1+\lambda} w \tag{3.11b}$$

Thus, there exists a two-parameter family of scaling solutions $\bar{\varphi}(\bar{x})$. The two parameters a and b determine the scale of the x and the φ axes.

The values of the parameters a and b are fixed as follows. First we discuss *nongelling systems*. In this case the choice of the unit of volume determines the value of the first moment of the scaling function:

$$\int_0^\infty dx\, x\varphi(x) = p_1 = 1 \tag{3.12}$$

We recall that we have chosen $p_1 = 1$ throughout this paper. Equation (3.12) imposes a first condition on the values of a and b. A second condition is obtained if we give a precise meaning to the words "mean cluster size." Different definitions of $s(t)$ correspond to different values of a and b. As an example, consider the following three definitions of the mean cluster size:

$$\begin{aligned} &\text{(i)} \quad s(t) = M_1(t)/M_0(t) \\ &\text{(ii)} \quad s(t) = M_2(t)/M_1(t) \\ &\text{(iii)} \quad s(t) = M_3(t)/M_2(t) \end{aligned} \tag{3.13a}$$

Insertion of the scaling form (1.2) with $\tau' = 2$ into (3.13a) shows that $M_1(t)/M_0(t) \sim s(t)\, p_1/p_0$ as $s(t) \to \infty$. Similarly, $M_2/M_1 \sim s(t)\, p_2/p_1$ and $M_3/M_2 \sim s(t)\, p_3/p_2$. Thus, the definitions (3.13a) impose upon $\varphi(x)$ the following restrictions:

$$\text{(i)} \quad p_1 = p_0, \qquad \text{(ii)} \quad p_2 = p_1, \qquad \text{(iii)} \quad p_3 = p_2 \tag{3.13b}$$

The two conditions (3.12) and (3.13b) fix the values of the parameters a and b. It has been tacitly assumed that all moments p_α are finite. In case the lower moments, such as p_0, diverge (see Section 4.4), higher moments should be used to obtain a consistent description of the scaling laws. Convergence of p_α is determined by the small-x behavior of $\phi(x)$, which is discussed in Section 4.4. *In gelling systems*, one relation between a and b is obtained if we give a precise definition of "mean cluster size." For gelling models Eq. (3.12) does not apply, since $p_1 = \infty$ in this case.

A different representation of the $\varphi(x)$ equation is obtained if we consider the Mellin transform of (3.8b). For all values of α with $p_\alpha < \infty$, multiplication of (3.8b) with x^α and integration over all x yields

$$w(1+\alpha-\tau')\, p_\alpha = \frac{1}{2}\int_0^\infty dx \int_0^\infty dy\, K(x, y)\, \varphi(x)\, \varphi(y)[(x+y)^\alpha - x^\alpha - y^\alpha] \tag{3.14}$$

It must be stressed that Eq. (3.14), in contrast to the assertions in Ref. 4–6, does *not* contain new information about $\varphi(x)$. We use it mainly to derive expressions for w in terms of the moments p_α for coagulation kernels $K(x, y)$ of a simple mathematical structure.

3.2. An Integral Equation for $\varphi(x)$

In this subsection we transform Eq. (3.8b) into an integral equation, the right-hand side of which is free of cancelling infinities and, furthermore, is strictly positive. This can be achieved by starting from (2.1). We first transform its lhs using mass conservation (2.2) and the scaling hypothesis (1.2):

$$-\sum_{j=1}^{k} j\dot{c}_j = \sum_{j=k+1}^{\infty} j\dot{c}_j = -s^{-\tau'-2}\dot{s} \sum_{j=k+1}^{\infty} [j^2\varphi'(j/s) + \tau' js\varphi(j/s)]$$

$$= -s^{1-\tau'}\dot{s}\int_x^\infty dy\, [\tau' y\varphi(y) + y^2\varphi'(y)] \tag{3.15a}$$

where $x = k/s(t)$. In deriving (3.15a) we have assumed that the integral $\int_x^\infty dy\, y\varphi(y)$ converges at its upper boundary. Similarly, we find for the rhs of (2.1)

$$s^{-2\tau'} \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} iK(i, j)\, \varphi(i/s)\, \varphi(j/s)$$

$$= s^{3+\lambda-2\tau'} \int_0^x du \int_{1-x}^\infty dv\, uK(u, v)\, \varphi(u)\, \varphi(v) \tag{3.15b}$$

Combination of (3.15a), (3.15b) and separation of the x and t dependences gives Eq. (3.8a) for $s(t)$, and for the scaling function:

$$-w\int_x^\infty dy\,(\tau' y\varphi + y^2\varphi') = \int_0^x du \int_{x-u}^\infty dv\, uK(u,v)\,\varphi(u)\,\varphi(v) \quad (3.16)$$

Equation (3.16) can also be derived by multiplication of Eq. (3.8b) with x, integration over x from z to ∞, and relabeling $z \to x$.

The advantage of Eq. (3.16) over (3.8b) is that cancelling infinities are absent in (3.16), that the rhs is strictly positive, and that spurious solutions, i.e., solutions with $p_1 = \infty$, are automatically excluded, as we shall see in Section 4. Multiplication of (3.16) with x^α and integration over all x gives again (3.14).

For nongelling systems, where $\tau' = 2$, the integrand in the lhs of (3.16) is a complete derivative, and (3.16) transforms into the following nonlinear integral equation:

$$wx^2\varphi(x) = \int_0^x du \int_{x-u}^\infty dv\, uK(u,v)\,\varphi(u)\,\varphi(v) \quad (3.17)$$

provided that $\varphi(x)$ satisfies the boundary condition $x^2\varphi(x) \to 0$ as $x \to \infty$. We want to point out that the boundary condition is a direct consequence of mass conservation. If this conservation law had not been used in the derivation of (3.16), then the lhs would have been replaced by $w\int_0^x dy\,(\cdots)$. In the nongelling case ($\tau' = 2$), this equation can also be integrated to give (3.17), provided $\varphi(x)$ satisfies the *different* boundary condition $x^2\varphi(x) \to 0$ as $x \to 0$. We return to this point in Section 4 in relation to an unphysical exact solution of (3.8b) that satisfies the latter, but not the former boundary condition.

4. NONGELLING SYSTEMS WITH $\lambda < 1$

This section is organized as follows. First we make the results of the previous sections explicit for nongelling systems with $\lambda < 1$. The nongelling systems with $\lambda = 1$ are a borderline case, treated separately in Section 6. In Section 4.1 we give some known exact results. Next we determine the large-x and the small-x behavior of the scaling function $\varphi(x)$. The large-x behavior of $\varphi(x)$ is calculated in Section 4.2. In Section 4.3 we sketch the method that will be used to investigate the small-x behavior of $\varphi(x)$. This leading behavior of $\varphi(x)$ as $x \downarrow 0$ in classes I–III is given in Section 4.4. In Sections 4.5 and 4.6 we calculate correction terms to the leading small-x behavior in classes II and III, respectively.

We start with a specification of some general results for nongelling systems, where the scaling function, according to Section 2, has the form

$$c_k(t) \xrightarrow{S} [s(t)]^{-2}\, \varphi(k/s(t)) \tag{4.1}$$

Since we have set the mass density equal to unity, it follows from (4.1) that $p_1 = 1$. This fixes one of the two scale parameters a and b [see (3.11)]. For $\tau' = 2$ Eq. (3.8a) gives the time development of the mean cluster size as

$$\dot{s}s^{-\lambda} = w; \qquad s(t) = [C + (1-\lambda)\, wt]^z \tag{4.2}$$

where the exponent z has the value $1/(1-\lambda)$. The scaling function $\varphi(x)$ satisfies Eq. (3.8b) with $\tau' = 2$:

$$-w(2\varphi + x\varphi') = \lim_{\varepsilon \downarrow 0} \left[\frac{1}{2} \int_{\varepsilon x}^{(1-\varepsilon)x} K(y, x-y)\, \varphi(y)\, \varphi(x-y) - \varphi(x) \int_{\varepsilon x}^{\infty} dy\, K(x, y)\, \varphi(y) \right] \tag{4.3}$$

or, alternatively, Eq. (3.17). We recall that, in the derivation of (3.17), it has been assumed that $x^2\varphi(x) \to 0$ as $x \to \infty$, which is to some extent equivalent to the condition that p_1 converges at its upper boundary.

4.1. Exact Results

For general homogeneous kernels, Eq. (4.3) or (3.17) cannot be solved exactly. Only in special nongelling models, such as $K(x, y) = 1$ and $K(x, y) = x + y$, is the solution of (4.3), (3.17) known in closed form. For $K(x, y) = 1$, the solution for $p_1 = 1$ is $\varphi(x) = (2w)^2\, e^{-2wx}$. The parameter w is fixed if we choose one particular definition of "mean cluster size." For example, if we choose $s(t) = M_2(t)/M_1(t)$, as in (3.13), part (ii), then $w = 1$. For the kernel $K(x, y) = x + y$, which is a special case with $\lambda = 1$ (see Section 6), one finds $\varphi(x) = (2\pi)^{-1/2}\, x^{-3/2} e^{-x/2}$, where the constants have also been fixed by choosing (3.13), part (ii) as a definition for $s(t)$. [Note that $w = 2p_1$ due to (3.14) for $\alpha = 2$.] Furthermore, exact but *unphysical* solutions of the form $\varphi(x) = Bx^{-1-\lambda}$ are found for all nongelling models of class I. These unphysical solutions violate the boundary condition $x^2\varphi(x) \to 0$ as $x \to \infty$, so that in this case $p_1 = \infty$. For kernels other than $K(x, y) = 1$ and $K(x, y) = x + y$, one cannot calculate the scaling function $\varphi(x)$ exactly. For general nongelling models, therefore, the large- and the small-x behavior of $\varphi(x)$ must be calculated self-consistently.

4.2. The Large-x Behavior

First, we consider the large-x behavior of the scaling function $\varphi(x)$. It is known[14,15] that for cluster sizes much larger than the mean cluster size, the distribution $c_k(t)$ in (1.1) falls off exponentially:

$$c_k(t) \sim a\dot{z}k^{-\theta}e^{kz} \qquad (k \to \infty) \tag{4.4a}$$

with $z < 0$, $\dot{z} > 0$, and (provided $\nu < 1$)

$$\theta = \lambda; \qquad a^{-1} = \frac{1}{2}\int_0^1 dy\, K(y, 1-y)[y(1-y)]^{-\theta} \tag{4.4b}$$

As far as the large-x behavior is concerned, we restrict ourselves to exponents $\nu < 1$. For kernels with $\nu = 1$ the results are more complicated[15] and will not be considered here. Due to (4.4a), (4.4b) it seems reasonable to assume that $\varphi(x)$ also decays exponentially as $x \to \infty$, namely

$$\varphi(x) \sim Ax^{-\theta}e^{-\delta x} \qquad (x \to \infty) \tag{4.5}$$

The Ansatz (4.5) is supported by the results for the exactly solvable models mentioned above, where $\theta = 0$ for $K(x, y) = 1$ and $\theta = 3/2$ for $K(x, y) = x + y$.

Insertion of the Ansatz (4.5) into Eq. (3.17) shows that

$$\begin{aligned} wx^2\varphi(x) &\sim (A/\delta)\int_0^x du\, u\varphi(u)\, K(u, x-u)(x-u)^{-\theta}\, e^{-\delta(x-u)} \\ &\sim (A^2/\delta)\, e^{-\delta x}\int_0^x du\, K(u, x-u)\, u^{1-\theta}(x-u)^{-\theta} \\ &\sim (A^2/2\delta)\, x^{2+\lambda-2\theta}e^{-\delta x}\int_0^1 du\, K(u, 1-u)[u(1-u)]^{-\theta} \qquad (x \to \infty) \end{aligned} \tag{4.6}$$

Comparison of the various factors on the lhs and rhs shows that the Ansatz (4.5) is consistent only if

$$\theta = \lambda \tag{4.7a}$$

and

$$w\delta/A = \frac{1}{2}\int_0^1 dy\, K(y, 1-y)[y(1-y)]^{-\lambda} \tag{4.7b}$$

The integral in (4.7b) converges if $\nu < 1$ [see (1.3)]. Thus, we have found the asymptotic ($x \to \infty$) behavior for all nongelling models of classes I–III, with the restriction that $\nu < 1$.

One may also investigate possible solutions of Eq. (3.13) with non-exponential large-x behavior, such as algebraic functions, $\varphi(x) \sim Ax^{-\theta}$, or stretched exponential behavior, $\varphi(x) \sim Ax^{-\theta}\exp(-\delta x^{\beta})$ with $0 < \beta < 1$. Substitution of these trial functions into Eq. (4.3), or (3.17) shows that such behavior is inconsistent. More precisely, one only finds consistent solutions of the form $\varphi(x) \sim Ax^{-1-\lambda}$, and these solutions are unphysical since $p_1 = \infty$. We further remark that the asymptotic behavior (4.5), (4.7a), (4.7b) agrees with the large-k behavior (4.4a), (4.4b) if we identify $z(t) = -\delta/s(t)$. This may be seen with the help of Eq. (4.2) for $\dot{s}(t)$. The constants δ and A play the role of the parameters a and b in the general solution $\bar{\varphi}(\bar{x}) = b\varphi(\bar{x}/a)$.

4.3. Small-x Behavior: Restrictions on Admitted Solutions

In this subsection we introduce the method used to investigate the small-x behavior of $\varphi(x)$. The advantage of this method is that the small-x behavior of $\varphi(x)$ may be studied systematically. As a result we find an explicit asymptotic form for $\varphi(x)$ ($x \downarrow 0$). This asymptotic form is qualitatively different in classes I–III.

The essential point in our arguments is that we restrict the class of allowed solutions to functions satisfying certain smoothness criteria, which are formulated in terms of the following ratio:

$$f(x, y) = \varphi(xy)/\varphi(x) \tag{4.8}$$

The reason is that, for large classes of functions $\varphi(x)$, the behavior of $f(x, y)$ is particularly simple as $x \downarrow 0$. As we shall see in Section 4.3, once $f(x, y)$ is known for $x \downarrow 0$, one may determine the detailed behavior of $\varphi(x)$ from Eq. (3.13). We restrict our study to the large class of functions $\varphi(x)$ that are smooth in the sense that $f(x, y)$ converges to a limit as $x \downarrow 0$, i.e., we assume that there exists a function $f(y)$ such that

$$\lim_{x \downarrow 0} f(x, y) = f(y); \qquad f(1) = 1 \tag{4.9}$$

In order to clarify the restriction imposed by (4.9), we give a few examples. The class of functions $\varphi(x)$ with the property (4.9) includes, for instance, algebraic behavior, dressed with possible logarithmic factors, i.e., $\varphi(x) \sim x^{-\tau}(-\log x)^{\beta}$ as $x \downarrow 0$, with τ and β arbitrary, or functions that vanish

exponentially rapidly as $x \downarrow 0$, such as $\varphi(x) \sim \exp(-x^{-1})$. Excluded are rapidly oscillating functions, such as $\varphi(x) \sim x^{-\tau}[1+\sin(1/x)]$.

We distinguish the two possibilities: $f'(1)$ is finite and $f'(1) = \infty$. If $f'(1)$ is finite, differentiation of (4.8) and (4.9) with respect to y gives

$$f'(y) = \lim_{x \downarrow 0}[x\varphi'(xy)/\varphi(x)] \tag{4.10a}$$

$$= f'(1) f(y)/y \tag{4.10b}$$

Integration of Eq. (4.10b) shows that $f(y)$ can only be a purely algebraic function, i.e.,

$$f(y) = y^{-\tau} \tag{4.11}$$

where $\tau \equiv -f'(1)$. The integration constant in (4.11) has been fixed by the requirement that $f(1) = 1$. The alternative case, where $\tau = -f'(1) = -\infty$, is more complicated, and will be discussed in Section 4.4.

The possible behavior of the scaling function $\varphi(x)$ admitted by the criteria (4.9) or (4.11) can be determined from (4.10a). If we set $y = 1$ in (4.10a), this equation can be integrated to yield

$$\log \varphi(x) \sim -\tau \log x \qquad (x \downarrow 0) \tag{4.12}$$

Thus, restricting the class of allowed $f(y)$ to *strictly* algebraic functions still admits scaling functions that are algebraic and dressed with additional factors, such as $(-\log x)^{\beta}$, that vary more slowly than any power of x.

4.4. The Leading Small-x Behavior (Classes I–III)

First we determine the small-x behavior in class I ($\mu > 0$). For this purpose we rescale the integral on the right of (3.13) by a factor x. The result may be expressed in terms of the function $f(x, y)$, defined in (4.8), as follows:

$$wx^2\varphi(x) = x^{3+\lambda}[\varphi(x)]^2 \int_0^1 dy \int_{1-y}^{\infty} dz\; yK(y, z)\, f(x, y)\, f(x, z) \tag{4.13}$$

We first look for solutions satisfying (4.11) with τ finite, and require that the integral in (4.13) converges as $x \downarrow 0$, i.e.,

$$1 + \nu < \tau < 2 + \mu \tag{4.14}$$

In this case Eq. (4.13) reduces for small x to

$$\varphi(x) \sim Bx^{-\tau} \quad (x \downarrow 0), \qquad \tau = 1 + \lambda, \quad B = w/J(1+\lambda) \tag{4.15}$$

The definition of $J(\tau)$ is given in (2.4b). Consistency requires that the value of τ found in (4.15) satisfies the inequalities (4.14). In all nongelling systems of class I these conditions are fulfilled since $\mu > 0$ and $\lambda = \mu + \nu < 1$. Thus, Eq. (4.15) gives the dominant small-x behavior of $\varphi(x)$.

Next we look for small-x solutions with $f(x, y) \to y^{-\tau}$ and

$$\tau \leqslant 1 + \nu \tag{4.16}$$

and obtain the small-x behavior in classes II and III. In this case, we split off the dominant contribution in the rhs of (3.17) as follows:

$$wx^2\varphi(x) = \int_0^x dy\, y^{1+\mu}\varphi(y) \int_{x-y}^{\infty} dz\, z^{\nu}\varphi(z) + R_1(x) \tag{4.17a}$$

The remainder $R_1(x)$ in (4.17a) is defined by

$$R_1(x) \equiv \int_0^x dy\, y\varphi(y) \int_{x-y}^{\infty} dz\, \varphi(z)[K(y, z) - y^{\mu}z^{\nu}] \tag{4.17b}$$

and has the property $R_1(x) = o[x^2\varphi(x)]$ as $x \downarrow 0$.

As a next step, we argue that the νth moment p_ν, defined in (2.13), is finite, i.e.,

$$h_\nu(x) \equiv \int_x^{\infty} dz\, z^{\nu}\varphi(z)$$

converges to $p_\nu < \infty$ as $x \downarrow 0$. In order to see that p_ν is indeed finite, we assume the opposite, namely that $h_\nu(x)$ diverges as $x \downarrow 0$. This could happen only if the exponent τ in (4.11) or (4.12) is equal to $1 + \nu$. In this case $h_\nu(x)$ diverges more slowly than any (negative) power of x, i.e., $h_\nu(xy)/h_\nu(x) \to 1$ as $x \downarrow 0$ for every fixed value of $y > 0$. As a consequence, Eq. (4.17) reduces to

$$wx^2\varphi(x) \sim x^{2+\mu}\varphi(x)\, h_\nu(x) \int_0^1 dy\, y^{1+\mu-\tau} \qquad (x \downarrow 0) \tag{4.18}$$

Since $h_\nu(x)$ diverges more slowly than any power of x, Eq. (4.18) is obviously inconsistent for all values of μ. We conclude that the assumption of a divergence of $h_\nu(x)$ as $x \downarrow 0$ leads to a contradiction. It follows that necessarily $p_\nu = h_\nu(0)$ is finite. As a consequence, Eq. (4.17) simplifies to

$$wx^2\varphi(x) = p_\nu \int_0^x dy\, y^{1+\mu}\varphi(y) + R_2(x) \tag{4.19a}$$

The remainder $R_2(x)$ is now given by

$$R_2(x) = R_1(x) - \int_0^x dy\, y^{1+\mu}\varphi(y) \int_0^{x-y} dz\, z^{\nu}\varphi(z) \qquad (4.19b)$$

and has the property $R_2(x) = o[x^2\varphi(x)]$ as $x \downarrow 0$.

The dominant small-x behavior of $\varphi(x)$ in classes II and III may now be obtained as follows. Dividing Eq. (4.19a) by $wx^2\varphi(x)$ yields

$$1 = w^{-1}p_{\nu}x^{\mu} \int_0^1 dy\, y^{1+\mu} f(x, y) + o(1) \qquad (x \downarrow 0) \qquad (4.20)$$

Recall that the constant w is strictly positive; cf. (3.8a). Before addressing classes II and III, we note that in class I (where $\mu > 0$) the rhs of (4.20) vanishes as $x \downarrow 0$ and consistent solutions with $\tau \leqslant 1 + \nu$ [see (4.16)] do not exist.

In class II, where $\mu = 0$, it follows from (4.20) that necessarily $f(x, y) \to y^{-\tau}$ as $x \downarrow 0$, with $\tau < \infty$ in order that the rhs of (4.20) converges to a positive constant. Substitution into (4.20) of the relation (4.11) and calculation of the integral shows that $\tau = 2 - p_{\lambda}/w$. Thus, in class II, we find that $\varphi(x)$ falls off algebraically, with an exponent τ that is related to integrals over $\varphi(x)$:

$$\log \varphi(x) \sim -\tau \log x \qquad (x \downarrow 0) \qquad (4.21a)$$

$$\tau = 2 - p_{\lambda}/w \qquad (4.21b)$$

Thus, we find an expression for the τ exponent in terms of the moment p_{λ} of the scaling function [defined in (2.13)] and the separation constant w [see (3.8a), (3.8b)]. It immediately follows from (3.11a), (3.11b) that the value (4.21b) for τ is *independent* of the parameters a and b, i.e., independent of the chosen scales of the x and φ axes. The correction terms to the leading behavior (4.21a), (4.21b) are calculated in Section 4.5.

As a simple illustration of this result, we consider the kernel $K(x, y) = x + y$ with degree of homogeneity $\lambda = 1$. We use the Mellin transform (3.14) with $\tau' = 2$ and $\alpha = 2$ to find that $w = 2p_1$. Since $p_1 = p_{\lambda}$ in this example, we deduce from (4.21b) that $\tau = 3/2$, in agreement with the explicit solution, already discussed in Section 4.1.

Finally, if $\mu < 0$ (class III), the prefactor x^{μ} in (4.20) diverges as $x \downarrow 0$. We conclude that within class III no solutions satisfying (4.9) with $\tau = -f'(1) = \text{finite}$ exist. We therefore study the only possibility left, $\tau = -f'(1) = -\infty$, so that the scaling function $\varphi(x)$ vanishes more rapidly than any power of x. In this case, the integral equation (4.19a) for the small-x behavior of $\varphi(x)$ in class III can be easily solved by converting it into a

differential equation. This can be done by differentiating (4.19a) with respect to x, yielding

$$wx^2\varphi'(x) \sim p_\nu x^{1+\mu}\varphi(x) \qquad (x \downarrow 0) \tag{4.22}$$

Integration gives for the dominant behavior in class III as $x \downarrow 0$

$$\varphi(x) = \exp(-p_\nu x^{-|\mu|}/|\mu|\, w + \cdots) \qquad (x \downarrow 0) \tag{4.23}$$

The result shows that for all models of class III, $\varphi(x)$ falls off exponentially rapidly as $x \downarrow 0$. Possible algebraic and constant factors in $\varphi(x)$ constitute less dominant asymptotic corrections and will be discussed in Section 4.6.

Thus, we have found the dominant small-x behavior of $\varphi(x)$ for the nongelling models of class I with $\lambda < 1$ and for the models of classes II and III. The restriction $\nu < 1$ in classes II and III that was imposed in Section 4.2 does not apply for the small-x behavior of $\varphi(x)$. The results of Sections 4.3 and 4.4 are valid for all models with $\lambda < 1$ and $\nu \leqslant 1$.

4.5. Subleading Small-x Behavior (Class II)

In the next subsections we try to determine asymptotic corrections to the dominant small-x behavior found in Section 4.4. In class I we did not succeed in finding its explicit form, or even its analytical structure. We return to this point in Section 7.

In class II we found the leading small-x behavior as $\varphi(x) \simeq x^{-\tau}$. The exponent τ given in (4.21b) is not known explicitly, but consistency requirements determine the bound (4.16), namely $\tau \leqslant 1 + \lambda$, where we used the equality $\lambda = \nu$ valid in class II ($\mu = 0$) due to (1.3b).

More details about the asymptotic ($x \downarrow 0$) behavior of $\varphi(x)$ can be obtained if we know the structure of the correction term $R_2(x)$ in (4.19b) for small x, which in turn requires a more detailed specification of the kernel $K(x, y)$ in (4.17b). Suppose $K(x, y)$ has the structure

$$K(y, z) = z^\nu + K_1\, y^{\mu_1} z^{\lambda - \mu_1} + \cdots \qquad (z \to \infty) \tag{4.24}$$

with $\mu_1 > 0$. In this case we distinguish three possibilities for the τ exponent in (4.21): $\tau \leqslant 1 + \lambda - \mu_1$, $1 + \lambda - \mu_1 < \tau < 1 + \lambda$, and $\tau = 1 + \lambda$, which will be discussed in this order.

We first estimate the remainder $R_2(x)$ in (4.19b), where the second term in the rhs is always of the order of $x^{3+\lambda-2\tau}$ as $x \downarrow 0$. The remaining term $R_1(x)$, defined in (4.17b), contains the integral

$$\int_{x-y}^{\infty} dz\, \varphi(z)[K(y, z) - z^\lambda] \sim K_1\, y^{\mu_1} \int_{x-y}^{\infty} dz\, \varphi(z)\, z^{\lambda - \mu_1} \tag{4.25}$$

Since y is small compared to z, we have approximated $K(y, z)$ in (4.25) by (4.24). Thus, if $\tau < 1 + \lambda - \mu_1$, we find for the rhs of (4.25) $K_1 y^{\mu_1} p_{\lambda-\mu_1}$, and we have the small-$x$ estimate

$$R_2(x) \sim K_1 p_{\lambda-\mu_1} \int_0^x dy\ y^{1+\mu_1} \varphi(y) \qquad (x \downarrow 0) \tag{4.26}$$

If $\tau > 1 + \lambda - \mu_1$, then both terms in (4.19b) give a contribution of the same order, and we find that

$$R_2(x) \sim I(\tau)\, x^{3+\lambda} [\varphi(x)]^2 \qquad (x \downarrow 0) \tag{4.27a}$$

with $I(\tau)$ given by

$$I(\tau) \equiv \int_0^1 dy\ y^{1-\tau} \int_{1-y}^{\infty} dz\ z^{-\tau} [K(y, z) - z^{\lambda}] - \int_0^1 dy\ y^{1-\tau} \int_0^{1-y} dz\ z^{\lambda-\tau} \tag{4.27b}$$

Finally, if $\tau = 1 + \lambda - \mu_1$, then the factor $p_{\lambda-\mu_1}$ in (4.26) is replaced by $B \log x$, with B defined by $\varphi(x) \sim B x^{-\tau}$ as $x \downarrow 0$.

With the use of Eqs. (4.26) and (4.27) for $R_2(x)$, we may now determine the detailed small-x behavior of $\varphi(x)$. Differentiation of (4.19a) in combination with (4.21b) gives an equation for $\varphi(x)$:

$$w x^2 \varphi'(x) + w\tau x \varphi(x) = R_2'(x) \tag{4.28}$$

This equation is valid for all x, and can be solved explicitly [at least formally, because $R_2(x)$ contains the unknown $\varphi(x)$]. The result is

$$\varphi(x) = x^{-\tau} \left[B + w^{-1} \int_0^x dy\ y^{\tau-2} R_2'(y) \right] \tag{4.29a}$$

where τ is given by Eq. (4.21b). As (4.29a) is an exact transformation of (3.17), it also holds for $x \to \infty$. In this limit the lhs of (4.29a) vanishes exponentially due to (4.5), so that the constant B is related to $R_2(y)$ as

$$B = -w^{-1} \int_0^{\infty} dy\ y^{\tau-2} R_2'(y) = -w^{-1}(2-\tau) \int_0^{\infty} dy\ y^{\tau-3} R_2(y) \tag{4.29b}$$

Consistency requires that B in (4.29b) is positive. The correction terms to the dominant small-x behavior of $\varphi(x)$ may readily be calculated from

(4.27a) with the use of (4.25) and (4.26). One finds that for small x, $\varphi(x)$ is given by

$$\varphi(x) = Bx^{-\tau}(1 + K_1 p_{\lambda-\mu_1} x^{\mu_1}/w\mu_1 + \cdots) \qquad (\tau < 1+\lambda-\mu_1) \tag{4.30a}$$

$$= Bx^{-\tau}(1 + BK_1 x^{\mu_1} \log x/w\mu_1 + \cdots) \qquad (\tau = 1+\lambda-\mu_1) \tag{4.30b}$$

$$= Bx^{-\tau}[1 + (3+\lambda-2\tau)\, BI(\tau)\, x^{1+\lambda-\tau}/w(1+\lambda-\tau) + \cdots]$$
$$(\tau > 1+\lambda-\mu_1) \tag{4.30c}$$

Finally, we consider possible solutions $\varphi(x)$ with $\tau = 1+\lambda$. In the derivation of (4.27) and (4.30c) we have assumed that $\tau < 1+\lambda$ holds, and for $\tau = 1+\lambda$, Eq. (4.30c) is obviously incorrect. From Section 4.4 we know that in principle solutions with $\tau = 1+\lambda$ could occur, provided that $p_\lambda < \infty$. The convergence of p_λ requires that the integration constant B in (4.29a) vanishes, i.e., $B = 0$. Partial integration of the integral in (4.29a) then shows that

$$\varphi(x) = w^{-1}x^{-1-\lambda}\left[x^{\lambda-1}R_2(x) + (1-\lambda)\int_0^x dy\, y^{\lambda-2}R_2(y)\right] \tag{4.31a}$$

For small x, $R_2(x)$ is determined by the *second* term in (4.19b). Qualitatively, this may be seen already in the expression (4.27), valid for $\tau < 1+\lambda$. If we take the limit $\tau \to 1+\lambda$ in (4.27b), then the second term diverges, whereas the first remains finite. Hence

$$R_2(x) \sim -\int_0^x dy\, y^{1+\mu}\varphi(y)\int_0^{x-y} dz\, z^\lambda \varphi(z)$$

$$\sim -(1-\lambda)^{-1}x^2\varphi(x)\int_0^x dy\, y^\lambda \varphi(y) \qquad (x \downarrow 0) \tag{4.31b}$$

In the derivation of (4.31b) we have used that $j(x) \equiv \int_0^x dy\, y^\lambda \varphi(y)$ vanishes as $x \downarrow 0$ more slowly than any power of x, so that $j(ux)/j(x) \to 1$ as $x \downarrow 0$ for all fixed u with $0 < u < 1$. Similarly, we used the property (4.11) of $\varphi(x)$, i.e., $\varphi(yx)/\varphi(x) \to y^{-1-\lambda}$ as $x \downarrow 0$. Combination of (4.31a), (4.31b) shows that $\varphi(x)$ is negative as $x \downarrow 0$, which is contradictory. We conclude that solutions with $\tau = 1+\lambda$ are excluded, i.e., that the exponent τ in class II satisfies the strict inequality $\tau < 1+\lambda$. From the result (4.29) it then follows that for all models in class II, the *behavior of* $\varphi(x)$ *is strictly algebraic* as $x \downarrow 0$. Within the class of slowly varying functions with the property (4.9), all other behavior is excluded.

4.6. Subleading Small-x Behavior (Class III)

Also here it is possible to determine systematically corrections to the dominant small-x behavior. We first consider the (more or less) general case. Next we discuss some special examples.

It is illustrative to start with kernels $K(y, z)$ that can be expanded in a power series as $z \to \infty$:

$$K(y, z) = \sum_{n=0}^{\infty} K_n y^{\mu_n} z^{\lambda - \mu_n} \qquad (z \to \infty) \tag{4.32}$$

with $K_0 = 1$ and $\mu_0 = \mu$. Most kernels in the literature have the property (4.32). The leading small-x behavior (4.23) in class III implies that, as $x \downarrow 0$, the first term in Eq. (4.3) is exponentially small relative to the second term. Thus, if we insert (4.32) into Eq. (4.3), we find that, for small x, $\varphi(x)$ satisfies the following equation:

$$w(2\varphi + x\varphi') \sim \varphi(x) \sum_{n=0}^{\infty} K_n x^{\mu_n} p_{\lambda - \mu_n} \qquad (x \downarrow 0) \tag{4.33}$$

where the correction terms to the rhs of (4.33) are exponentially small. Integration of Eq. (4.33) yields for $\varphi(x)$

$$\varphi(x) \sim C x^{-2} \exp\left[-\sum_{n=0}^{\infty} K_n (x^{\mu_n}/\mu_n w)\, p_{\lambda - \mu_n} \right] \qquad (x \downarrow 0) \tag{4.34}$$

The prefactor $C > 0$ remains undetermined. If $\mu_n = 0$ for some value of n, then x^{μ_n}/μ_n in (4.34) is replaced by $\log x$.

Next we show that in the limit $\mu \uparrow 0$, the small-x behavior in class III crosses over to the known behavior (4.29a), (4.29b) in class II. To do this, we give a formal solution for $\varphi(x)$ for general coagulation kernels in class III. Differentiation of Eq. (4.19a) gives an equation from which $\varphi(x)$ can be solved in terms of $R_2(x)$. The result is

$$\varphi(x) = -(wx^2)^{-1} \exp\left[\frac{p_v}{\mu w} (x^{\mu} - 1) \right] \int_x^{\infty} dy \exp\left[-\frac{p_v}{\mu w} (y^{\mu} - 1) \right] R_2'(y) \tag{4.35}$$

The constant factors $\exp(\pm p_v/\mu w)$ in (4.35) have been inserted for convenience only. Insertion of these factors clearly shows that the expression (4.35) for $\varphi(x)$ in class III reduces to the result (4.29) in class II if the kernel $K(x, y)$ is modified in such a way that the exponent μ vanishes ($\mu \uparrow 0$).

For definiteness we consider a kernel of the form (4.32) with $\mu < 0$ and $\mu_1 > 0$. In this case, the small-x behavior (4.26) of $R_2(x)$ implies that the

integral in (4.35) is convergent. Thus, we find that for small x, (4.35) reduces to

$$\varphi(x) \sim Bx^{-2} \exp[(p_\nu/\mu w)(x^\mu - 1)] \qquad (x \downarrow 0) \tag{4.36a}$$

with the prefactor B given by

$$B = -w^{-1} \int_0^\infty dy\, R_2'(y) \exp[-(p_\nu/\mu w)(y^\mu - 1)] \tag{4.36b}$$

If the coagulation kernel (4.32) approaches the kernels of class II, i.e., if $\mu \uparrow 0$, then (4.36) reduces to the leading small-x behavior in (4.29).

Finally, we consider as an example several model kernels with $\mu < 0$:

$$\begin{aligned} K_1(x, y) &= (xy)^\mu \\ K_2(x, y) &= x^\mu + y^\mu \\ K_3(x, y) &= (x^\mu + y^\mu)(x^{-\mu} + y^{-\mu}) \\ K_4(x, y) &= x^\mu y^\nu + y^\mu x^\nu \qquad (\nu > 0) \end{aligned} \tag{4.37}$$

For $\mu = -1/3$, the kernel $K_3(x, y)$ corresponds to Brownian coagulation. The kernels (4.37) all have the form (4.32), so that for small x, $\varphi(x)$ is of the form (4.34). The constant w in (4.34) can be expressed in terms of the moments p_α of $\varphi(x)$ with the use of (3.14), where we choose $\alpha = 0$. For the kernels K_1, K_2 one finds, respectively, $w_1 = (p_\mu)^2/2p_0$, $w_2 = p_\mu$, $w_3 = (p_0^2 + p_\mu p_{-\mu})/p_0$, and $w_4 = p_\mu p_\nu / p_0$. Insertion of these values into (4.34) finally gives for the corresponding asymptotic behavior of $\varphi(x)$ as $x \downarrow 0$

$$\varphi_1(x) \sim C_1 x^{-2} \exp(2x^\mu p_0/\mu p_\mu) \tag{4.38a}$$

$$\varphi_2(x) \sim C_2 x^{-1} \exp(x^\mu p_0/\mu p_\mu) \tag{4.38b}$$

$$\varphi_3(x) \sim C_3 x^{-\gamma} \exp(-x^{-|\mu|} p_{-\mu}/|\mu|\, w_3 + x^{|\mu|} p_\mu/|\mu|\, w_3) \tag{4.38c}$$

$$\varphi_4(x) \sim C_4 x^{-2} \exp(-x^{-|\mu|} p_\nu/|\mu|\, w_4 + x^\nu p_\mu/\nu w_4) \tag{4.38d}$$

The exponent γ in (4.38c) is related to the moments p_α of $\varphi_3(x)$ as $\gamma = 2p_\mu p_{-\mu}/p_0 w_3$.

5. ASYMPTOTIC SOLUTIONS FOR GELLING SYSTEMS ($\lambda > 1$)

In gelling systems, where the average cluster size diverges in finite time, the scaling Ansatz has the form (1.2) with $\tau' = \tau$, i.e.,

$$c_k(t) \xrightarrow{S} s(t)^{-\tau} \varphi(k/s(t)) \tag{5.1}$$

The "critical" exponent is $\tau = (\lambda + 3)/2$ due to (2.5a). The time dependence of $s(t)$ is given by (3.8a), i.e.,

$$\dot{s}s^{\tau-\lambda-2} = w; \qquad s(t) = [\sigma w(t_c - t)]^{-1/\sigma} \tag{5.2}$$

where we have introduced the critical exponent $\sigma = 1 + \lambda - \tau = \frac{1}{2}(\lambda - 1)$. In this section we study the equation for the scaling function (3.16), i.e.,

$$-w\int_x^\infty dy\,(\tau y\varphi + y^2\varphi') = \int_0^x du \int_{x-u}^\infty dv\, uK(u, v)\,\varphi(u)\,\varphi(v) \tag{5.3}$$

The solution of this equation again contains two arbitrary constants, i.e., if $\varphi(x)$ is a solution, then $b\varphi(x/a)$ is also a solution [see (3.11a), (3.11b)].

In order to study how the parameters a and b in (3.11) are fixed in gelling systems, we consider first the special model $K(x, y) = xy$, which has $\lambda = 2$. In this case the exact solution of Eq. (5.3) has in general the form

$$\varphi(x) = Bx^{-5/2}e^{-x/a} \tag{5.4a}$$

where the two parameters (B, a) play the role of (b, a) in (3.11). Since in the present case the solutions of Smoluchowski's equation for a given initial distribution are known exactly,[17] one can determine how the two parameters depend on the initial conditions. The results are the following. The parameter a in (5.4a) is determined only by the definition of "mean cluster size" and does not depend on the initial conditions. For instance, the choice $s(t) = M_3(t)/M_2(t)$ or $s(t) = M_4(t)/M_3(t)$ corresponds to $a = 2$ or $a = 2/3$, respectively. Thus, the choice of $s(t)$ fixes the scale of the x axis. The parameter B in (5.4a) is determined by the initial conditions, and is independent of the definition of $s(t)$:

$$B = \{[M_2(0)]^3/2\pi M_3(0)\}^{1/2} \tag{5.4b}$$

The constant w in (5.3) can be calculated from (3.14) for $\alpha = 2$ as $w = 2p_2 = 2(a\pi)^{1/2}B$. Thus, w depends on the initial conditions and on the definition of $s(t)$.

For different kernels with $\lambda > 1$ the general solution of (5.3) has the form $\varphi(x) = Bx^{-\tau}\Phi(x/a)$, with $\Phi(0) = 1$ and B and a arbitrary. The value of the parameter a, i.e., the scale of the x axis, is again fixed by the definition of $s(t)$. The value of B or of w depends in general on the initial conditions. However, the explicit dependence of B (or w) on the initial conditions remains undetermined, since the solution of the initial value problem (1.1) for general homogeneous kernels is not known. We further mention that we cannot fix the constant B by setting $p_1 = 1$, as we did in the nongelling case, because here $p_1 = \infty$. The reason is that only a

negligible fraction of the total mass is contained in the scaling region, as already discussed at the end of Section 2.

The large-x behavior of $\varphi(x)$ is determined along the same lines as in Section 4. For $k \to \infty$ (with $t < t_c$ fixed), the cluster size distribution $c_k(t)$ falls off exponentially.[14] Hence, we assume that for large x, $\varphi(x)$ has the form (4.5) also for gelling systems. Substitution of (4.5) into (5.3) leads to exactly the same result (4.7a), (4.7b) as for nongelling systems. The reason is that the second term in the lhs of (3.8b) is dominant as $x \to \infty$ in gelling and nongelling systems. Thus, the value of τ' is irrelevant for the leading asymptotic behavior of $\varphi(x)$ as $x \to \infty$. As an immediate consequence, we have that the large-x behavior (4.5) with (4.7a), (4.7b) is also for gelling systems, in agreement with the large-k result (4.4).

The dominant small-x behavior of $\varphi(x)$ is of the form $\varphi(x) \sim Bx^{-\tau}$, with $\tau = (\lambda + 3)/2$. As a consequence, the rhs of Eq. (5.3) converges to a positive constant as $x \downarrow 0$, so that (5.3) reduces to

$$-w \int_0^\infty dy\, (\tau y\varphi + y^2\varphi') = B^2 J((\lambda+3)/2) \tag{5.5}$$

with $J(\tau)$ given in (2.4b).

Subleading asymptotic corrections can be obtained by assuming that corrections to the dominant small-x behavior are of algebraic type:

$$\varphi(x) = x^{-\tau}[B + \gamma(x)] \tag{5.6a}$$

with

$$\gamma(x) \sim B_1 x^\alpha \qquad (x \downarrow 0, \alpha > 0) \tag{5.6b}$$

From (4.5) it follows that for large x, $\gamma(x) \to -B$.

The value of α can be determined by subtracting (5.5) from (5.3). The result is

$$\begin{aligned} w &\int_0^x dy\, (\tau y\varphi + y^2\varphi') \\ &= \int_0^x du \int_{x-u}^\infty dv\, uK(u,v)[\varphi(u)\,\varphi(v) - B^2(uv)^{-\tau}] \\ &= B \int_0^x du \int_{x-u}^\infty dv\, uK(u,v)(uv)^{-\tau}[\gamma(u) + \gamma(v) + B^{-1}\gamma(u)\,\gamma(v)] \end{aligned} \tag{5.7}$$

The lhs of Eq. (5.7) can easily be evaluated for small x with the use of the Ansatz (5.6a), (5.6b):

$$\text{LHS}(5.7) \sim w\alpha B_1 \int_0^x dy\, y^{1-\tau+\alpha} \qquad (x \downarrow 0) \tag{5.8a}$$

The rhs can be evaluated as follows. The quadratic term $\gamma(u)\gamma(v)$ is negligible with respect to $\gamma(v)$, since $\gamma(u) \to 0$ as $u \downarrow 0$. Moreover, the first term in the rhs, corresponding to $\gamma(u)$, is proportional to x^α, which, according to (5.8a), is negligible with respect to the lhs of Eq. (5.7). Thus, the dominant contribution comes from the $\gamma(v)$ term in the rhs of (5.7), yielding

$$\text{RHS}(5.7) \sim B \int_0^x du\, u^{1-\tau} \int_{x-u}^{\infty} dv\, K(u, v)\, v^{-\tau}\gamma(v)$$

$$\sim B \int_0^x du\, u^{1+\mu-\tau} \int_0^{\infty} dv\, v^{\nu-\tau}\gamma(v) \qquad (x \downarrow 0) \qquad (5.8b)$$

In the derivation of (5.8b) we first replaced the lower bound of the v integral by $v = 0$. The relative error made in this way vanishes as x^α for $x \downarrow 0$. The next step is to use the property (1.3b) for $K(u, v)$ with $u \ll v$. Combination of (5.8a), (5.8b) and differentiation with respect to x finally shows that (5.6a), (5.6b) is consistent if

$$\alpha = \mu \qquad (5.9a)$$

and

$$B_1 = (B/w\mu) \int_0^{\infty} dv\, v^{\nu-\tau}\gamma(v) \qquad (5.9b)$$

Thus, we have determined the first correction to the leading small-x behavior.

We add the following comment. In principle it cannot be excluded that, in some special model, the integral in (5.9b) and hence the prefactor B_1 for $\alpha = \mu$ vanishes. If by coincidence the rhs of (5.9b) should vanish, then the small-x behavior of $\gamma(x)$ is determined by the correction terms to the dominant behavior (1.3b) of $K(u, v)$. For instance, if $K(u, v)$ is of the form (4.32) as $v \to \infty$, then Eq. (5.8b) is replaced by

$$\text{RHS}(5.7) \sim K_1 B \int_0^x du\, u^{1+\mu_1-\tau} \int_0^{\infty} dv\, v^{\lambda-\mu_1-\tau}\gamma(v) \qquad (x \downarrow 0) \quad (5.10)$$

so that instead of (5.9a), (5.9b) one finds

$$\alpha = \mu_1 \qquad (5.11a)$$

$$B_1 = (K_1 B/w\mu_1) \int_0^{\infty} dv\, v^{\lambda-\mu_1-\tau}\gamma(v) \qquad (5.11b)$$

However, we emphasize that, in general, B_1 in (5.9b) does *not* vanish. For instance, in simple models, such as $K(x, y) = (xy)^\omega$ with $\frac{1}{2} < \omega \leqslant 1$, it can be verified that B_1 is nonvanishing for $\alpha = \mu$. Thus, Eq. (5.6) with α and B_1 given by (5.9) represents the generic behavior of $\varphi(x)$ as $x \downarrow 0$. This concludes our study of the asymptotic properties of the scaling function $\varphi(x)$ in gelling models.

6. A SPECIAL CASE: $\lambda = 1$

In this section we discuss coagulation kernels with a degree of homogeneity exactly equal to unity, which are *nongelling* according to the discussion of Section 2.

Within the class of kernels with $\lambda = 1$ we distinguish models with $\mu = 0$ (class II) and $\mu > 0$ (class I). In class II ($\mu = 0$), the results of Section 4 are valid also for models with $\lambda = \nu = 1$. The reason is that in class II, the τ exponent satisfies $\tau < 1 + \nu = 1 + \lambda = 2$ [see (4.16)], and hence $p_1 < \infty$ in this case. All restrictions imposed in class II are satisfied. The time dependence of $s(t)$ for $\lambda = 1$ is given by $s(t) \sim s_0 e^{wt}$ if $t \to \infty$, as follows from (4.2).

In *class I* the solution valid for $\lambda < 1$ breaks down for $\lambda = 1$, since $c_k(t) \sim s(t)^{-2} \varphi(k/s(t))$ with $\varphi(x) \sim Bx^{-2}$ $(x \downarrow 0)$ implies that the sol mass diverges as $s \to \infty$:

$$M_1(t) \sim \int_{s^{-1}}^{\infty} dx\, x\varphi(x) \sim B \log s \to \infty \qquad (s \to \infty) \tag{6.1}$$

which contradicts the conservation law $M_1(t) = 1$. We infer from (6.1) that for class I models with $\lambda = 1$, the scaling Ansatz (4.1) is *incorrect.* In Appendix B we show how the scaling law (4.1) can be modified. Below, we summarize the results.

The method for obtaining scaling solutions of Smoluchowski's equation if $\lambda = 1$ is based on the known large-time behavior of the cluster size distribution. The relevant results are summarized in Appendix A. It is known[19,20] that in class I models as $t \to \infty$, for a fixed value of the cluster size k, the ratio $c_k(t)/c_1(t)$ approaches a finite, nonvanishing limiting value b_k. The constants b_k satisfy the recursion relation (A.2), from which the asymptotic behavior may be calculated. For $\lambda = 1$ the result is

$$b_k \sim [E_1/2J(2)]\, k^{-2} \log k \qquad (k \to \infty) \tag{6.2}$$

with E_1 and $J(\tau)$ given in (A.2b) and (2.4b), respectively. The appropriate scaling Ansatz turns out to be

$$c_k(t) \xrightarrow{S} c_1(t)\, b_k \Phi(k/s(t)) \tag{6.3}$$

with the initial value of $\Phi(x)$ given by $\Phi(0)=1$. Obviously, for a fixed value of k, the scaling Ansatz (6.3) gives the correct large-time behavior, since $k/s(t)\to 0$, and $\Phi(k/s(t))\to 1$ as $t\to\infty$.

Substitution of the scaling Ansatz (6.3) into the normalization of the sol mass, $\sum kc_k(t)=1$, shows (see Appendix B) that the time dependence of the monomer concentration $c_1(t)$ is given by

$$c_1(t)\sim [4J(2)/E_1][\log s(t)]^{-2} \qquad (t\to\infty) \tag{6.4}$$

Substitution of the Ansatz (6.3) in combination with (6.4) into Smoluchowski's equation (2.1) yields first an equation for the mean cluster size:

$$s^{-1}\dot{s}\log s = 2w; \qquad s(t)=s_0\exp[2(wt)^{1/2}] \tag{6.5}$$

Second, we find an equation for the scaling function $\Phi(x)$. If we introduce

$$\varphi(x)\equiv x^{-2}\Phi(x); \qquad \Phi(0)=1 \tag{6.6}$$

then $\varphi(x)$ satisfies Eq. (3.17), where the separation constant w has a fixed value, $w=J(2)$. The small-x behavior of $\varphi(x)$ is trivially given by $\varphi(x)\sim x^{-2}$ as $x\downarrow 0$. The large-x behavior is given by (4.5), (4.7a), and (4.7b). By construction, the large-time behavior of $c_k(t)$ agrees with the scaling solution for small values of the argument $x=k/s(t)$. Similarly, the large-k solution at fixed t agrees with (6.3) in the scaling limit if $x\gg 1$.

7. SUMMARY AND DISCUSSION

We start with a summary of our results. In this paper we have studied scaling solutions of Smoluchowski's coagulation equation for homogeneous kernels with an exponent $\nu<1$. The homogeneous kernels constitute a large class of *mathematical models* for the reaction rates $K(i,j)$, which includes all *physical kernels* used in the literature (see, e.g., Ref. 3). Within the class of homogeneous coagulation kernels, we distinguish gelling ($\lambda>1$) and nongelling ($\lambda\leqslant 1$) models. In *gelling models* the mean cluster size $s(t)$ diverges at a finite time t_c as $s(t)\propto (t_c-t)^{-1/\sigma}$, where the critical exponent σ has the value $\sigma=\frac{1}{2}(\lambda-1)$. The scaling function $\varphi(x)$ falls off algebraically as $x\downarrow 0$, $\varphi(x)\sim Bx^{-\tau}$, with the critical exponent $\tau=\frac{1}{2}(\lambda+3)$. In *nongelling models* the mean cluster size diverges as $t\to\infty$. If $\lambda<1$ one finds that $s(t)\propto t^z$ with $z=1/(1-\lambda)$. Alternatively, for $\lambda=1$, $\log s(t)\propto t$ if $\mu=0$ (class II), or $\log s(t)\propto\sqrt{t}$ if $\mu>0$ (class I). The scaling function $\varphi(x)$ in nongelling systems falls off algebraically for small x in classes I and II, with $\tau=1+\lambda$ in class I, and τ related to integrals over $\varphi(x)$ in class II. In class III, $\varphi(x)$ falls off exponentially fast as $x\downarrow 0$. For large x values, the

scaling function $\varphi(x)$ in all gelling and nongelling models falls off exponentially, as in (4.5).

The scaling solutions studied in this paper have been investigated for small and large values of the scaling argument $x = k/s(t)$ with the use of self-consistent methods. Therefore, we should emphasize that the *existence of scaling solutions* and the *approach to the scaling solutions* from arbitrary initial conditions have not been proven in general. Such a proof has been given only for the exactly solvable models $K(x, y) = xy$, $K(x, y) = x + y$, and $K(x, y) = 1$.

For the *nongelling* models of *class I*, we have not been able to find the first correction to the leading small-x behavior (4.15). Here the question of existence of certain classes of solutions presents itself. We cannot exclude the possibility that in this case no solution $\varphi(x)$ of Eq. (4.3) or (3.17) exists that satisfies the physical requirement that the total mass be finite, $p_1 < \infty$.

For many nongelling models in class III and for special models in class II, including $K(x, y) = x^\omega + y^\omega$ with $0 < \omega \leqslant 1$, one may construct the *exact* scaling function $\varphi(x)$ in the form of a series representation, so that in classes II and III the question of existence of scaling solutions seems rather academic. The same remark applies to the gelling models of class I, where for special cases, such as $K(x, y) = (xy)^\omega$ with $\frac{1}{2} < \omega \leqslant 1$, one is also able to give an exact solution of the $\varphi(x)$ equation. The results concerning exact solutions will be published elsewhere.[18] In any model, apart from the three exactly solvable models mentioned above, the question of approach to the scaling solution from arbitrary initial conditions remains open.

Next we discuss the relation between the results from the scaling theory and the results obtained in the limits $k \to \infty$ with t fixed, and $t \to \infty$ with k fixed. In Section 4.2 we have shown for nongelling systems with $\lambda < 1$ that if $s(t) \to \infty$ the behavior (4.4) for $k \gg s(t)$ coincides with the prediction (4.5), (4.7a), (4.7b) from the large-x behavior of the scaling function theory. This shows that the regions of validity of the two limiting solutions—(1) first $k \to \infty$, next $s(t) \to \infty$, and (2) first k and $s(t) \to \infty$, with $x = k/s(t)$ fixed, next $x \to \infty$—are overlapping. The same result holds for nongelling systems with $\lambda = 1$ (see Appendix B) and for gelling systems ($\lambda > 1$).

The relation between the scaling function results and the large-time results of Leyvraz[19] and of van Dongen and Ernst[20] is discussed next. We consider only class I, since in classes II and III the behavior of $c_k(t)$ as $t \to \infty$ with k fixed is nonuniversal, i.e., depends on the initial distribution $c_k(0)$. Within class I we consider only the nongelling models ($\lambda \leqslant 1$), since for gelling models the scaling limit is relevant at t_c, not at $t = \infty$. For the nongelling models of class I the ratio $c_k(t)/c_1(t)$ approaches a finite, nonvanishing limit as $t \to \infty$, independent of the initial conditions: $c_k(t)/$

$c_1(t) \to b_k$. The relevant large-time results are summarized in Appendix A. For class I models with $\lambda < 1$ the behavior of $c_1(t)$ as $t \to \infty$ and of b_k for $k \gg 1$ is given in (A.3) and in (A.7a), (A.8), respectively. Combination of these results yields the same expression for $c_k(t)$ as the scaling function results (4.1) and (4.2) if the small-x behavior of $\varphi(x)$ is given by (4.15). For class I models with $\lambda = 1$, the scaling law (6.3) is constructed in such a way that for $t \to \infty$ it agrees with the large-time results (A.1), (A.3), and (A.9). We conclude that for $c_k(t)$ in the nongelling models of class I, there are overlapping regions of validity of the two limits: (1) first $t \to \infty$, next $k \to \infty$, and (2) k, $s(t) \to \infty$, with $k/s(t)$ fixed, and next $x \downarrow 0$.

Finally we mention some numerical results concerning the scaling functions in class III ($\mu < 0$), which have been discussed in Section 4.6. Swift and Friedlander[6] calculated the shape of the scaling function for Brownian coagulation, which is supposedly described by the kernel $K_3(x, y)$ in (4.37) if the exponent is given by $\mu = -1/3$. They found as an estimate for the exponent γ in (4.38c) the value $\gamma \simeq 1.06$. New numerical results have recently been obtained by Meesters and Ernst,[21] who calculated the scaling function $\varphi(x)$ for the kernels K_1, K_2, and K_4 in (4.37) for various values of the exponent μ. These authors numerically study the crossover of the scaling function from class III behavior to class II behavior as the exponent μ vanishes: $\mu \uparrow 0$. Analytically the nature of this crossover is obvious from (4.35), at least for the kernels K_1 and K_4.

APPENDIX A. SUMMARY OF LARGE-TIME RESULTS

For all models of class I ($\mu > 0$), Leyvraz[19] and van Dongen and Ernst[20] have shown that the ratio of the k-mer concentration to the monomer concentration, $c_k(t)/c_1(t)$, approaches a positive constant b_k as $t \to \infty$, with the cluster size k kept fixed:

$$c_k(t)/c_1(t) \to b_k \qquad (t \to \infty) \tag{A.1}$$

The constants b_k satisfy the following recursion relation:

$$E_1 \sum_{j=1}^{k} j b_j = \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} iK(i, j)\, b_i b_j \tag{A.2a}$$

where the factor E_1 is given by

$$E_1 \equiv \sum_{j=1}^{\infty} K(1, j)\, b_j \tag{A.2b}$$

It is obvious from (A.1) that the initial condition for (A.2) is $b_1 = 1$. The

time dependence of the monomer concentration $c_1(t)$ can be determined by inserting (A.1) into Eq. (1.1) for $k=1$. This yields $\dot{c}_1 = -E_1(c_1)^2$, or

$$c_1(t) \sim (E_1 t)^{-1} \qquad (t \to \infty) \tag{A.3}$$

The asymptotic behavior of b_k in (A.2) for all gelling and nongelling models can readily be determined as follows. We assume that as $i, k \to \infty$, with $u = i/k$ fixed, the solution b_k of (A.2) has the rather general property

$$b_i/b_k = b_{uk}/b_k \to f(u) \qquad (k \to \infty) \tag{A.4}$$

where $f(u)$ is a continuous function of u. Insertion of (A.4) into (A.2a) shows that for large k, (A.2a) reduces to

$$E_1 \sum_{j=1}^{k} j b_j \sim C k^{3+\lambda} (b_k)^2 \qquad (k \to \infty) \tag{A.5a}$$

where the constant C is given by

$$C \equiv \int_0^1 du \int_{1-u}^{\infty} dv\, uK(u, v) f(u) f(v) \tag{A.5b}$$

Differentiation of Eq. (A.5) with respect to k gives the following differential equation for b_k:

$$\frac{d}{dk}\left[k^{(3+\lambda)/2} b_k\right] \sim \frac{E_1}{2C} k^{-(1+\lambda)/2} \qquad (k \to \infty) \tag{A.6}$$

Integration of Eq. (A.6) is elementary. For gelling systems ($\lambda > 1$) the result is

$$b_k \sim B k^{-\tau} \qquad (k \to \infty) \tag{A.7a}$$

where the exponent τ and the prefactor B are given by

$$\tau = (\lambda + 3)/2; \qquad B = \left[E_1 \sum_{j=1}^{\infty} j b_j / J(\tau)\right]^{1/2} \tag{A.7b}$$

In the derivation of (A.7) we have used that $f(u) = u^{-\tau}$ and $C = J(\tau)$, with $J(\tau)$ defined in (2.4b). For nongelling systems with $\lambda < 1$ one finds again the form (A.7a), now with

$$\tau = 1 + \lambda; \qquad B = E_1/[(1-\lambda) J(\tau)] \tag{A.8}$$

Finally, if $\lambda = 1$, integration of Eq. (A.6) gives

$$b_k \sim [E_1/2J(2)]\, k^{-2} \log k \qquad (k \to \infty) \tag{A.9}$$

where we used $f(u) = u^{-2}$ and $C = J(2)$.

APPENDIX B. SCALING FUNCTION RESULTS FOR $\lambda = 1$

For nongelling models in class I with $\lambda = 1$, the large-time behavior (A.1) suggests that the cluster size distribution $c_k(t)$ approaches a scaling solution of the form

$$c_k(t) \xrightarrow{\text{S}} c_1(t)\, b_k \Phi(k/s(t)) \tag{B.1}$$

with $\Phi(0) = 1$. More generally, Eq. (B.1) should hold for *all* nongelling ($\lambda \leqslant 1$) models in class I, and, in fact, if $\lambda < 1$, Eq. (B.1) in combination with Eqs. (A.3), (A.7a), and (A.8) is equivalent to the conventional scaling form (4.1). For $\lambda = 1$, the asymptotic behavior of b_k is calculated in Eq. (A.9) of Appendix A.

The relation between the monomer concentration $c_1(t)$ in (B.1) and the mean cluster size $s(t)$ can be determined from the requirement that the sol mass is equal to unity. With $x \equiv k/s(t)$ we have

$$\begin{aligned} 1 = \sum_{k=1}^{\infty} k c_k &\sim c_1 \sum_{k=1}^{\infty} k b_k \Phi(x) \\ &\sim [E_1/2J(2)]\, c_1 \sum_{k=1}^{\infty} k^{-1} (\log k)\, \Phi(x) \end{aligned} \tag{B.2}$$

If we substitute into (B.2) the relation

$$\log k = \log x + \log s \tag{B.3}$$

then we can approximate (B.2) as

$$\begin{aligned} 1 &\sim [E_1/2J(2)]\, c_1 \int_{s^{-1}}^{\infty} dx\, x^{-1} (\log x + \log s)\, \Phi(x) \\ &\sim [E_1/4J(2)]\, c_1 (\log s)^2 \qquad [s(t) \to \infty] \end{aligned} \tag{B.4}$$

In the limit $s \to \infty$ this implies (6.4) for $c_1(t)$.

Equation (B.1), in combination with (6.2) and (6.4), implies that the usual scaling hypothesis (4.1) for nongelling models is slightly modified. In the scaling region, where x in (B.3) is kept fixed, so that

$$\log k \sim \log s \qquad (s \to \infty) \tag{B.5}$$

Eq. (B.1) reduces to

$$c_k(t) \sim 2(s \log s)^{-2} (\log k)\, \varphi(x) \tag{B.6a}$$

$$\sim 2(s^2 \log s)^{-1}\, \varphi(x) \qquad [s(t) \to \infty] \tag{B.6b}$$

where we have introduced the scaling function $\varphi(x) \equiv x^{-2}\Phi(x)$. Comparison of (B.6) with (4.1) shows that (B.6) contains an extra factor $(\log s)^{-1}$. We further note that for $\lambda = 1$, all mass is contained in cluster sizes much smaller than $s(t)$, just as in *gelling* systems. A similar argument as in (B.2)–(B.4) shows that for all $\varepsilon > 0$, the mass contained in clusters with size $k \leqslant \varepsilon s(t)$ approaches unity as $s(t) \to \infty$, i.e., $M^{(\varepsilon s)}(t) \to 1$ $(s \to \infty)$.

Next we derive an equation for the scaling function $\Phi(x)$ or, equivalently, for $\varphi(x)$. We proceed along similar lines as in (3.15a), (3.15b) and we substitute the Ansatz (B.1) into the lhs of Eq. (2.1):

$$-\sum_{j=1}^{k} j\dot{c}_j = \sum_{j=k+1}^{\infty} j\dot{c}_j = \sum_{j=k+1}^{\infty} jb_j[\dot{c}_1 \Phi(x) - kc_1 \dot{s}\Phi'(x)/s^2] \tag{B.7}$$

Substitution into (B.7) of the asymptotic behavior (6.2) of b_k and use of (6.4) and (B.5) shows that the second term in the rhs of (B.7) is dominant as $s \to \infty$:

$$-\sum_{j=1}^{k} j\dot{c}_j \sim [E_1/2J(2)]\, c_1 \dot{s} s^{-1} \log s \int_x^{\infty} dy\, \Phi'(y)$$

$$\sim (2\dot{s}/s \log s)\, \Phi(x) \tag{B.8a}$$

Similarly, replacing $c_k(t)$ by the scaling Ansatz (B.1) and using (B.5), we find for the rhs of (2.1):

$$\sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} iK(i, j)\, c_i c_j$$

$$\sim (c_1)^2 \sum_{i=1}^{k} \sum_{j=k-i+1}^{\infty} iK(i, j)\, b_i b_j \Phi(i/s)\, \Phi(j/s)$$

$$\sim 4(\log s)^{-2} \int_0^x du \int_{x-u}^{\infty} dv\, uK(u, v)\, \varphi(u)\, \varphi(v) \tag{B.8b}$$

Combination of (B.8a), (B.8b) and separation of the x and t dependences finally yields Eq. (6.5) for $s(t)$ and Eq. (3.17) for $\varphi(x)$. If we take the limit $x \downarrow 0$ in Eq. (3.17) and use the fact that $\Phi(0) = 1$, we obtain an explicit expression for the separation constant w in (3.17), namely $w = J(2)$. The time dependence of $c_1(t)$ as obtained from (6.4) and (6.5) agrees with the result (A.3) from the large-time solution.

The *small-x behavior* of $\varphi(x) = x^{-2}\Phi(x)$ is obviously given by $\varphi(x) \sim x^{-2}$ $(x \downarrow 0)$. We have not been able to determine corrections to the dominant term, as was the case for all nongelling models of class I. The large-x behavior of the solution $\varphi(x)$ of (3.17) is determined in (4.5), (4.7).

Finally, we discuss the relation between the scaling forms (B.6a), (B.6b) and the large-time (fixed-k) behavior and large-k (fixed-t) behavior of $c_k(t)$. Clearly, both forms (B.6a) and (B.6b) are equivalent in the scaling limit k, $s \to \infty$, $x = k/s$ fixed. Equation (B.6a), or rather Eq. (B.1), has the additional advantage that it gives the correct large-time behavior if we take the limit $s \to \infty$ with k fixed. This implies that the large-time result (A.1) is valid also in the scaling limit, provided that $x = k/s \ll 1$. Similarly, there is a common region of validity for the scaling result and the results (4.4a), (4.4b) obtained in the limit $k \to \infty$, s fixed. This can be seen by inserting into (4.4) the Ansatz $z(t) = -\delta/s(t)$ and taking the scaling limit, where $x = k/s(t) \gg 1$ is kept fixed. This concludes our remarks concerning nongelling class I models with $\lambda = 1$.

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