Irreversible aggregation kinetics: Power-law exponents from series

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The kinetics of irreversible aggregation are studied using power series in time for general sum and product kernels of the type $(i^\alpha+j^\alpha)$ and $(ij)^\alpha$. Assuming a power-law form for the asymptotic behavior of the first moment of the cluster distribution, $M_0 \sim t^{-\gamma}$, we are able to determine the exponent γ by inverting the series to give t as a function of the first moment. Exact solutions are known for $\alpha=0$ and 1. Our numerical method gives γ as a function of α for α in the range from 0 to 1 for the sum kernel. For the product kernel we are able to determine γ near $\alpha=0$ and 1, but a power-law form does not seem to fit the series well in the midrange near $\alpha=\frac{1}{2}$. For the product kernel we clearly detect the onset of the gelation transition at $\alpha=\frac{1}{2}$.

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I. INTRODUCTION

We consider the kinetics of the irreversible aggregation of clusters described by the general reaction

$$(i)+(j)\rightarrow(i+j)\ , \tag{1.1}$$

where the letters indicate the number of monomer units in a cluster. Ignoring the effects of excluded volume and assuming mass-action kinetics (i.e., reaction-limited aggregation), the time evolution of the system is given by the Smoluchowski equation [1]

$$\frac{dc_k}{d(at)}=\frac{1}{2}\sum_{i+j=k}K_{ij}c_ic_j-c_k\sum_{j=1}^{\infty}K_{jk}c_j\ , \tag{1.2}$$

where c_k indicates the concentration of a k-mer. We treat the case of monodisperse initial conditions

$$c_k(0)=\delta_{k1}\ , \tag{1.3}$$

i.e., the system is all monomer (of unit concentration) at $t=0$. The moments of the distribution are defined as

$$M_n=\sum_{k=1}^{\infty}k^nc_k\ . \tag{1.4}$$

M_0 is the net concentration of clusters, while M_1 is the total number of monomer units in the system (usually conserved, i.e., $M_1=1$).

We will treat rate constants (kernels) of the form

$$K_{ij}=1\ \ \text{(constant)}\ , \tag{1.5}$$

$$K_{ij}=(i^\alpha+j^\alpha)/2\ \ \text{(sum)}\ , \tag{1.6}$$

$$K_{ij}=(ij)^\alpha\ \ \text{(product)} \tag{1.7}$$

for the range

$$0\le\alpha\le1\ . \tag{1.8}$$

We will refer to the case $\alpha=1$ as either the simple sum or simple product kernel, as appropriate.

Our purpose here is to solve (1.2) as an exact series in powers of time for arbitrary α in the range given above and then, by appropriate manipulation of the series, using techniques developed to determine critical exponents, evaluate the exponent for the power law

$$M_0\sim t^{-\gamma}\ . \tag{1.9}$$

We note that we will take the scale factor in (1.2) as $a=2$, giving the relation between our time (t) and the common convention (t'):

$$2t=t'\ . \tag{1.10}$$

We do this so as always to give the beginning series for $M_0(t)$ as

$$M_0(t)=1-t+\cdots\ . \tag{1.11}$$

It is for this reason that we have also inserted the factor of 2 in our definition of the sum kernel in (1.6).

For the constant kernel $K_{ij}=1$, (1.2) was solved in 1918 by Smoluchowski [1]. In 1962 McLeod [2] solved (1.2) for the simple product kernel $K_{ij}=ij$. McLeod found that his solution was valid only for $0\le t\le\frac{1}{2}$ [using our t in (1.10) with M_2 becoming infinite at $t=\frac{1}{2}$]. $M_2\rightarrow\infty$ indicates that the mean-square cluster size goes to infinity; this singularity has since been interpreted as the onset of gelation (formation of infinite clusters), and the time of the onset of gelation is referred to as t_g. The general characteristics of the gelation phenomena are

$$M_1(t\le t_g)=1,\ \ M_1(t>t_g)<1\ , \tag{1.12}$$

$$M_2(t=t_g)=\infty\ . \tag{1.13}$$

From (1.12) one sees that the gelation time is the onset of the lack of conservation of monomer units. For $t\le t_g$ the system is referred to as existing in the sol phase, while for $t>t_g$, it is in the gel phase. Using power series in time, we have access only to the behavior in the sol phase up to the sol-gel transition time. We will be able to use the series to determine t_g as a function of α, i.e., detect the onset of gelation (the sol-gel transition). For finite t_g, Eq.

(1.9) must be appropriately modified [see (5.6) and (5.7)].

Of crucial importance for the use of a series solution of (1.2) is the question of the existence of the series. For the simple product kernel McLeod [2] determined that for the range of α given in (1.8), there was a unique, analytic solution near $t=0$. However, for $\alpha>1$ he showed that the radius of convergence was zero. Van Dongen [3] interpreted the case of $\alpha>1$ as leading to instantaneous gelation. For the case of the sum kernel White [4] has proved that for α in the range of (1.8), there exists a global (all-t) solution that is well behaved (i.e., no gelation). Leyvraz and Tschudi [5] have proved for the product kernel that $\alpha\geq\frac{1}{2}$ is a necessary condition for gelation. They comment [6] that for the product kernel there is no proof of gelation occurring in the range $\frac{1}{2}<\alpha<1$, but that heuristic arguments favor it. Leyvraz showed [7] for a diagonal product kernel $K_{ij}=i^{\omega}\delta_{ij}$ that there is gelation at a finite time for $\omega>1$ (i.e., $K_{ii}=i^{2\alpha}$ gelation if $\alpha>\frac{1}{2}$). Ziff [8] has speculated that the diagonal kernels are a sufficient diagnostic of gelation and that gelation will occur if $\alpha>\frac{1}{2}$; however, Buffet and Werner [9] have given a counterexample where for a particular diagonal-only kernel, there is gelation, and the addition of off-diagonal kernels destroys it.

For purposes of having a few reference systems with which to compare our series solutions, it is useful to review the exact solutions of (1.2). For the simple product kernel $K_{ij}=ij$, as we have mentioned already, McLeod [2] gave a solution for $t\leq\frac{1}{2}$. Leyvraz and Tschudi [6] interpreted the singularity at $t=t_g$ as the gelation phenomenon and gave a solution both for $t<t_g$ and $t>t_g$ for the kernel

$$K_{ij}=(Ai+B)(Aj+B)\ ;$$

they find that in general $t_g=\{2A(A+B)\}^{-1}$. Later, Van Dongen and Ernst [10] gave a general solution for the bilinear kernel

$$K_{ij}=A+B(i+j)+Cij\ ,$$

which for appropriate choices of A, B, and C gives the constant, simple sum, and simple product kernels. They give the general solution of (1.2) with the bilinear kernel in the form

$$c_k(t)=A(t)N_k\xi(t)^k \tag{1.14}$$

and present explicit recipes for the calculation of $A(t)$, $\xi(t)$, and a recursion relation for the N_k. All of the classic exact results can be obtained from the moment equations that they give:

$$\frac{dM_0}{dt}=-(AM_0^2+2BM_0M_1+CM_1^2)\quad(\text{all } t)\ , \tag{1.15}$$

$$\frac{dM_1}{dt}=0,\quad M_1=1\quad(t<t_g)\ , \tag{1.16}$$

$$\frac{dM_2}{dt}=2(A+2BM_2+CM_2^2)\quad(t<t_g)\ . \tag{1.17}$$

Taking $B=C=0$ and $A=1$, we get the constant kernel; taking $A=0$, $B=\frac{1}{2}$, and $C=0$, we get the simple sum kernel; and taking $A=B=0$ and $C=1$, we get the simple product kernel. One readily finds the following.

constant kernel (all t):

$$M_0=\frac{1}{1+t},\quad M_1=1,\quad M_2=1+2t\ ; \tag{1.18}$$

simple sum (all t):

$$M_0=e^{-t},\quad M_1=1,\quad M_2=e^{2t}\ ; \tag{1.19}$$

simple product ($t\leq\frac{1}{2}$):

$$M_0=1-t,\quad M_1=1,\quad M_2=\frac{1}{1-2t}\ ; \tag{1.20}$$

simple product ($t>\frac{1}{2}$):

$$M_0=\frac{1}{4t},\quad M_1=\frac{1}{2t},\quad M_2=\infty\ . \tag{1.21}$$

We note that for the simple product kernel, M_2 goes to infinity at the finite time $t=t_g=\frac{1}{2}$ (for the constant kernel and the simple sum kernel, M_2 goes to infinity at infinite time, i.e., $t_g=\infty$).

The detailed distributions are the following.

constant kernel (all t):

$$c_k(t)=t^{k-1}/(1+t)^{k+1}\ ; \tag{1.22}$$

simple sum (all t):

$$\begin{aligned}c_1(t)&=e^{-t}e^{-(1-e^{-t})}\ ,\\ c_2(t)&=e^{-t}(1-e^{-t})e^{-2(1-e^{-t})}\ ,\\ c_3(t)&=\tfrac{3}{2}e^{-t}(1-e^{-t})^2e^{-3(1-e^{-t})}\ ;\end{aligned} \tag{1.23}$$

simple product ($t\leq\frac{1}{2}$):

$$c_k(t)=\frac{k^{k-2}}{k!}(2t)^{k-1}e^{-2kt}\ ; \tag{1.24}$$

simple product ($t>\frac{1}{2}$):

$$c_k(t)=c_k(t_g)/2t\ . \tag{1.25}$$

In 1988 Kokholm [11] gave a simple proof of the global existence and uniqueness of the solution for the simple product kernel with monodisperse initial conditions. Lu [12] has solved the case of the general bilinear kernel with polydisperse initial conditions, while Treat [13] has also treated the bilinear kernel (with $C=0$) for the case of general initial conditions.

Several authors have treated the case where higher-order reaction terms are incorporated in the model. Jiang and Gang [14] included both second- and third-order kernels of the form $K_{ij}=ij$ and $K_{ijk}=ijk$, giving explicit expressions for the cluster size distribution for monodisperse initial conditions. For the general nth-order process (but one order only) with kernels of the form $K_{ij\ldots}=k_ik_j\ldots$, Jiang, Gang, and BenKun [15] discussed the critical properties and universality, but did not give a general solution. For the case of an nth-order process with either a constant or a simple sum kernel, Karpivsky [16] gives a general solution.

II. TIME-POWER SERIES SOLUTION

We assume a time-power series solution to (1.2):

$$c_k = \sum_{n=0}^{\infty} A_{kn} t^n / n! \ . \tag{2.1}$$

Using (2.1) in (1.2) gives a set of recursion relations [17] for the A_{kn}. For irreversible aggregation $M_0(t)$ will drop from $M_0=1$ at $t=0$ to $M_0=0$ at $t=\infty$, as illustrated in Fig. 1(a). We introduce the variable

$$y(t)=1-M_0(t) \tag{2.2}$$

with the time variation illustrated in Fig. 1(b). Formally, one has

$$y=\sum_{n=1}^{\infty} a_n t^n \ , \tag{2.3}$$

where the a_n are obtained through some finite value of n by the recursion process. Inverting the series (2.3) gives

$$t=\sum_{n=1}^{\infty} b_n y^n \ . \tag{2.4}$$

For the power-law behavior of (1.9) one has (assuming $t_g=\infty$)

$$t \sim \left[\frac{1}{1-y}\right]^{1/\gamma} \ . \tag{2.5}$$

The behavior of (2.4) or (2.5) is illustrated in Fig. 1(c). The reason for this transformation is that $t=t(y)$ goes to infinity at $y=1$ (as, for example, do the heat capacity and compressibility at the critical point), and hence we can use the techniques developed to determine critical exponents. Song and Poland [18] have successfully used the approach outlined above to treat diffusion-limited aggregation and annihilation in lattice gases, and Poland [19] has treated the growth of Eden clusters in a similar manner.

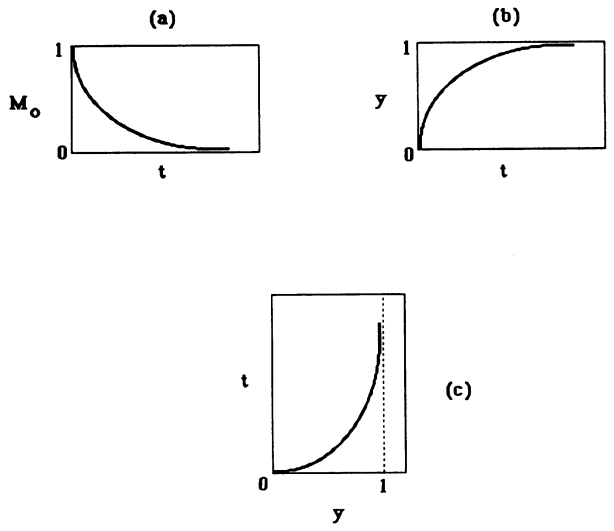


FIG. 1. (a) Schematic variation of M_0, the total concentration of aggregates, as a function of time. (b) Schematic variation of the function $y=1-M_0$ as a function of time. (c) Part (b) when inverted to give t as a function of y; the dotted line is the asymptote at $y=1$.

If y_g is the radius of convergence of the series (i.e., the singularity of interest is the one closest to the origin), then the ratios

$$r_n = b_n / b_{n-1} \tag{2.6}$$

of the (2.4) series are asymptotic [20] to

$$r_n \sim y_g^{-1}\left[1+\frac{1}{n}\left[\frac{1}{\gamma}-1\right]\right] \ . \tag{2.7}$$

For $y_g=1$, one has

$$1/\gamma = 1-n(1-r_n) \ . \tag{2.8}$$

Alternatively, one can use the Padé technique [20], giving

$$\frac{1}{\gamma}=(1-y)\frac{\partial \ln t(y)}{\partial \ln y} \ , \tag{2.9}$$

forming Padé approximants to the derivative.

III. SUM KERNEL

As an example of how the procedure outlined in Sec. II works, we treat the case of the sum kernel of (1.6) with $0 \le \alpha \le 1$. White [4] has proved that there is no gelation in this range, so we expect the power-law behavior of (1.9) in the whole range. At the extreme values of α, we have

$$M_0 \sim t^{-1} \ (\alpha=0), \quad M_0=e^{-t} \ (\alpha=1) \ . \tag{3.1}$$

The $\alpha=1$ result is equivalent to $t=-\ln(1-y)$, which gives $1/\gamma=0$ in the ratio formula of (2.8). Thus we expect that the exponent γ in the power law of (1.9) will vary from 1 to infinity over the range $\alpha=0$ to 1, or that $1/\gamma$ will vary from 1 to zero over the same interval.

For the case of $\alpha=0.5$, the series $M_0(t)$ through ten terms is given by

$$\begin{aligned} M_0(t)=1-t+0.7929t^2-0.5756t^3+0.3992t^4 \\ -0.2693t^5+0.1783t^6-0.1166t^7 \\ +0.0755t^8-0.0486t^9+0.0310t^{10}+\cdots \ , \end{aligned} \tag{3.2}$$

while the series for $t(y)$ is

$$\begin{aligned} t(y)=y+0.7929y^2+0.6818y^3+0.6096y^4 \\ +0.5578y^5+0.5181y^6+0.4865y^7 \\ +0.4605y^8+0.4385y^9+0.4197y^{10}+\cdots \ . \end{aligned} \tag{3.3}$$

The key as to whether or not this method will work is how well behaved the $t(y)$ series is. All of the $t(y)$ series that we have obtained have coefficients of uniform sign that vary monotonically in magnitude, as illustrated in (3.3).

Applying (2.7) to successive pairs of ratios from (3.3) gives the following series of estimates of y_g and $1/\gamma$:

$$y_g = 1.0063,\ 1.0029,\ 1.0018,\ 1.0012,\ 1.0009,\ 1.0007,\ 1.0006,\ 1.0004, \ldots , \tag{3.4}$$

$$1/\gamma = 0.596,\ 0.587,\ 0.583,\ 0.580,\ 0.579,\ 0.577,\ 0.576,\ 0.575, \ldots . \tag{3.5}$$

Clearly, y_g is approaching the value $y_g = 1$ rapidly, and the estimates of $1/\gamma$ seem to be monotonically approaching a limit. If we assume $y_g = 1$ exactly, we can use (2.8) to obtain the following series of estimates of $1/\gamma$:

$$1/\gamma = 0.586,\ 0.579,\ 0.577,\ 0.575,\ 0.574,\ 0.573,\ 0.572,\ 0.571, \ldots . \tag{3.6}$$

So with some confidence we take

$$1/\gamma = 0.57 \pm 1 \quad (\alpha = 0.5) \tag{3.7}$$

and

$$M_0 \sim t^{-1.75} . \tag{3.8}$$

The ratios for the function $t = t(y)$ as a function of $1/n$ are shown in Fig. 2 for various values of α in the range $\alpha = 0$ to 1. For all values of α shown, the ratios give linear plots [indicating that the power-law form of (1.9) is very closely obeyed for all t]. For all values of α, the ratios extrapolate to the expected value $1/y_g = 1$. The values of $1/\gamma$ obtained from the slopes are shown in Fig. 3 as a function of α and, as expected, we have a smooth variation of $1/\gamma$ from 1 to 0.

We note that $1/\gamma(\alpha)$ is approximated by the following simple relation:

$$\frac{1}{\gamma} = \frac{1-\alpha}{1-\alpha/4} = \begin{cases} 1 & (\alpha = 0) \\ \frac{4}{7} = 0.571 & (\alpha = \frac{1}{2}) \\ 0 & (\alpha = 1) . \end{cases} \tag{3.9}$$

IV. PRODUCT KERNEL

From the comments made in the Introduction, we expect the following behavior for the product kernel of (1.7) with $0 \le \alpha \le 1$:

$$y_g = 1 \quad \text{for } 0 \le \alpha \le \tfrac{1}{2} ,$$

$$y_g < 1 \quad \text{for } \tfrac{1}{2} < \alpha \le 1 , \tag{4.1}$$

$$y_g = \tfrac{1}{2} \quad \text{for } \alpha = 1 .$$

The last result follows from the fact that for $\alpha = 1$, $M_0 = 1 - t$ and $t_g = \frac{1}{2}$; hence $y_g = \frac{1}{2}$.

Whatever the exact functional form of t as a function of y, if the singularity at the gelation transition determines the radius of convergence, then $r_n \to y_g^{-1}$ as $1/n \to 0$. The ratios r_n of (2.6) for the function $t = t(y)$ for the product kernel are shown in Fig. 4 for various values of α. For $\alpha < \frac{1}{2}$ the ratios extrapolate to $y_g^{-1} = 1$, as expected. For the example shown with $\alpha > \frac{1}{2}$, i.e., $\alpha = 0.9$, the r_n extrapolate smoothly to $y_g^{-1} = 1.56$ ($y_g = 0.64$), which is approaching the known limit $y_g = \frac{1}{2}$ for $\alpha = 1.0$. The values of y_g can be obtained either from the extrapolation of the ratios or by the use of Padé approximants; the values obtained from the two methods agree closely. The values of $y_g(\alpha)$ obtained from Padé approximants are shown in Fig. 5(a). One sees that the conjectures concerning the behavior of $y_g(\alpha)$ given in (4.1) are borne out. We find that $y_g(\alpha = \frac{1}{2}) = 0.977$; within the accuracy of our methods, we cannot say that this number is not exactly 1.

For $y_g = 1$, one has $t_g = \infty$. As y_g drops in value from $y_g(\alpha = \frac{1}{2}) \cong 1$ to $y_g(\alpha = 1) = \frac{1}{2}$, t_g drops from $t_g(\alpha = \frac{1}{2}) = \infty$ to $t_g(\alpha = 1) = \frac{1}{2}$. In that range the series $t = t(y)$ converges to a finite limit at the singularity $y = y_g$. The values of t_g obtained from extrapolating the $t(y_g)$ series are given (plotted as $1/t_g$) in Fig. 4(b); we assume that $t_g(\alpha = \frac{1}{2}) = \infty$.

Thus, from the $t = t(y)$ series we are able to confirm the conjecture that there is a gelation transition at a finite time for the case of the product kernel in the range $\frac{1}{2} < \alpha \le 1$. From the series we can determine the behavior of both $y_g(\alpha)$ and $t_g(\alpha)$, as shown in Fig. 5.

For $\alpha \le \frac{1}{2}$ the form of (2.5) represents a strong singularity ($t \to \infty$ as $y \to 1$) and hence is easy to study using series methods. The straight lines in Fig. 4(a) for the cases $\alpha = 0$, 0.1, and 0.2 are drawn using the values of $1/\gamma$ obtained from the Padé approximants to the $t = t(y)$ series. One sees that the ratios are nicely asymptotic to these lines. The values of $1/\gamma$ for $\alpha = 0$, 0.1, and 0.2 are shown in Fig. 6 and one sees that $1/\gamma(\alpha)$ decreases with increasing α (as was the case for the sum kernel, as shown in Fig. 3). For higher values of α, the ratios and Padé approximants obtained from the $t = t(y)$ series become less straightforward to interpret. Part of the problem is that for $\alpha > \frac{1}{2}$, t_g is finite at y_g and hence is more difficult to abstract from the series (no quantity goes to infinity). Thus, in order to continue our analysis, we turn to a

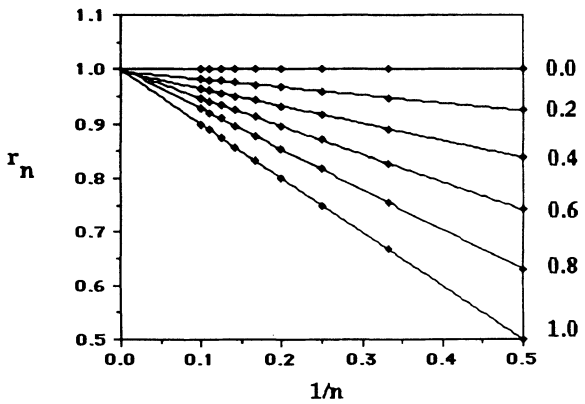


FIG. 2. Ratio plots r_n of (2.6) as a function of $1/n$ obtained from the function $t = t(y)$ for the sum kernel of (1.6). The appropriate values of α for each curve are indicated. The ratios all extrapolate to $y_g = 1$ at $1/n = 0$.

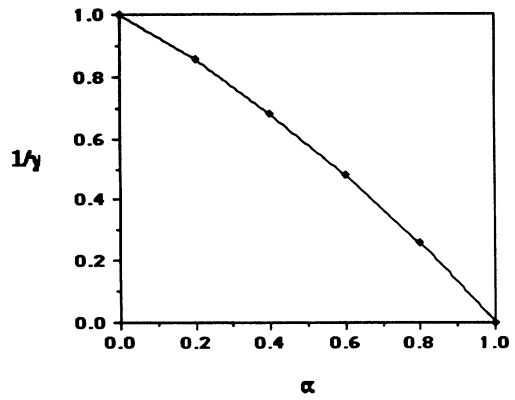


FIG. 3. The exponent $1/\gamma$ for the sum kernel as a function of α obtained from the slopes of the ratio plots in Fig. 2.

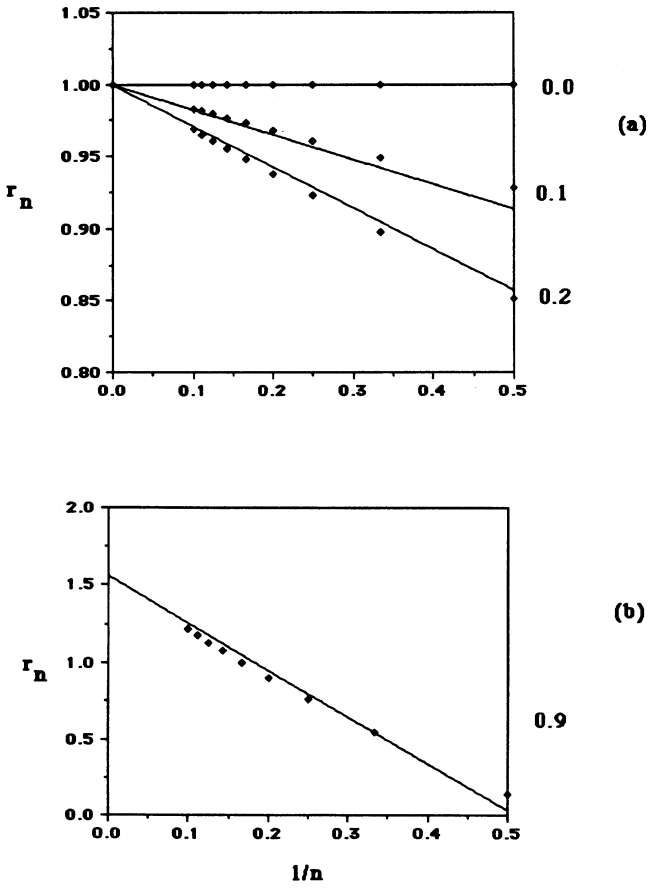
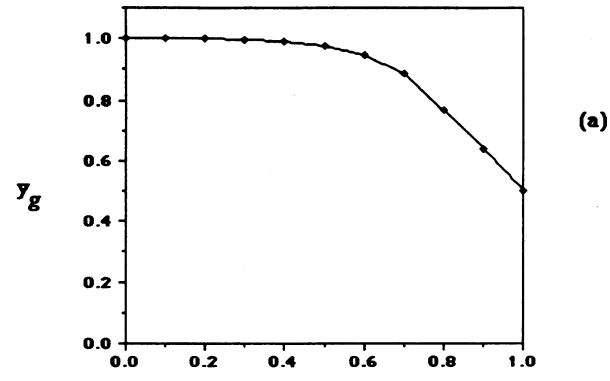


FIG. 4. Ratio plots r_n of (2.6) as a function of $1/n$ obtained from the function $t=t(y)$ for the product kernel of (1.7). The appropriate values of α for each curve are indicated. For $\alpha<\frac{1}{2}$ the ratios extrapolate to $y_g=1$; for the cases $\alpha=0$, 0.1, and 0.2, the straight lines were constructed using the slopes and intercepts obtained from Padé approximants to the series. For the case $\alpha=0.9$, one has $y_g<1$ $(1/y_g=1.56)$; for this case the straight line was constructed using y_g and $1/\gamma$ from the functions $M_2(t)$ and $M_2(y)$.



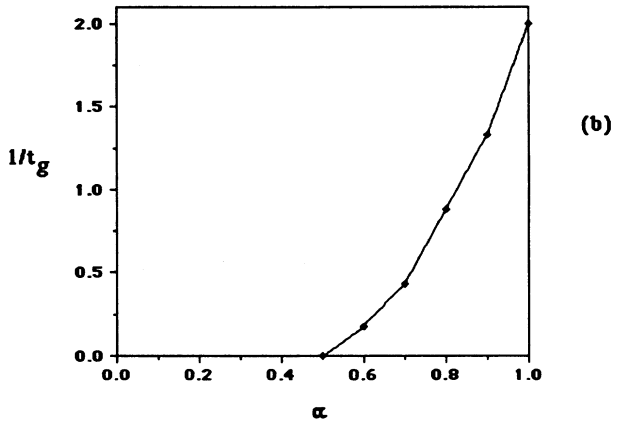


FIG. 5. The locus of the gelation transition as a function of α for the product kernel. The gelation concentration expressed as y_g $(=1-M_0)$ was obtained from Padé approximants to the $t=t(y)$ series. The gelation time t_g was obtained from the series $t_g=t(y_g)$; the point at $\alpha=0.5$ assumes that $t_g\to\infty$ at that value of α.

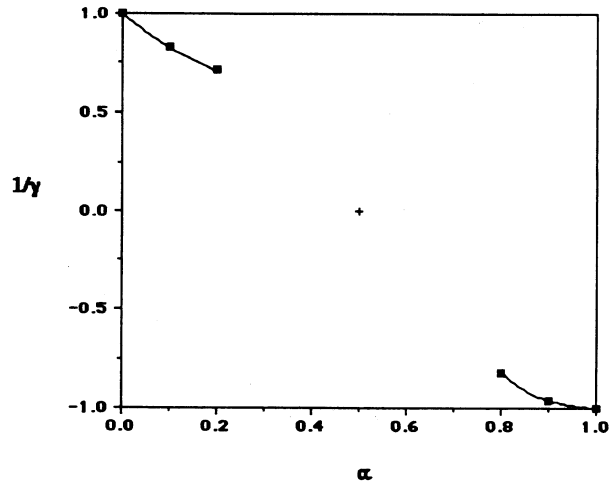


FIG. 6. The exponent $1/\gamma$ [defined in (2.5)] for the product kernel as a function of α. The points near $\alpha=0$ were determined from Padé approximants to the series $t=t(y)$. The points near $\alpha=1$ were obtained by combining the exponents for $M_2(t)$ and $M_2(y)$.

function that is always infinite at the gelation transition, the second moment M_2.

V. BEHAVIOR OF M_2

A discussion of the exponents associated with M_2 is given by Ziff, Ernst, and Hendriks [21]. A diagnostic of the gelation transition is the fact that $M_2(t)\to\infty$ as $t\to t_g$. Given the power series in time for M_0 and M_2, one can then construct the y series ($y=1-M_0$) for M_2. Introducing the variables

$$\Delta t=(1-t/t_g),\quad \Delta y=(1-y/y_g)\ , \tag{5.1}$$

we expect singularities in $M_2(t)$ and $M_2(y)$ of the form

$$M_2\sim\left[\frac{1}{\Delta t}\right]^{\nu_t},\quad M_2\sim\left[\frac{1}{\Delta y}\right]^{\nu_y}, \tag{5.2}$$

The known forms for $M_2(t)$ for select values of α are given in (1.18)–(1.21). For $M_2(y)$ one has the following results:

$$M_2=\left[\frac{1+y/y_g}{1-y/y_g}\right]$$

(sum and product kernel; $\alpha=0$; $y_g=1$) , (5.3)

$$M_2=\left[\frac{1}{1-y/y_g}\right]^2 \text{ (sum kernel; } \alpha=1;\ y_g=1)\ , \tag{5.4}$$

$$M_2=\left[\frac{1}{1-y/y_g}\right] \text{ (product kernel; } \alpha=1;\ y_g=\tfrac{1}{2})\ .$$

(5.5)

For the sum kernel one sees that $\nu_y(\alpha=0)=1$ and $\nu_y(\alpha=1)=2$; thus, we expect a continuous variation of ν between these two limiting values. For the product kernel we have $\nu_y(\alpha=0)=1$ and $\nu_y(\alpha=1)=1$. We note from (1.6) and (1.7) that the diagonal kernels are identical for the sum kernel at $\alpha=1$ and the product kernel at $\alpha=\frac{1}{2}$, i.e., $K_{ii}=i$ for both. Thus we expect that the behavior for these two cases will be very similar (the off-diagonal kernels are different), and we anticipate that ν_y will vary from 1 to 2 as α is increased from 0 to $\frac{1}{2}$ and then decrease again to 1 as α goes to 1.

To calculate the values of ν_y, we use the ratio method of (2.8). For the sum kernel the ratios for $M_2(y)$ are shown in Fig. 7 for various values of α [the cases of $\alpha=0$ and 1 are, of course, given exactly in (5.3) and (5.4)]. Analogous data for $M_2(y)$ are shown for the product kernel in Fig. 8(b). The variation of $\nu_y(\alpha)$ for the two kernels is shown in Fig. 9 and one sees that our conjectures are borne out. As mentioned earlier, we expect the case of $\alpha=\frac{1}{2}$ for the product kernel to be analogous to the case of $\alpha=1$ for the sum kernel. Since $\nu_y=2$ exactly at $\alpha=1$ for the sum kernel, we anticipate the same value of the case $\alpha=\frac{1}{2}$ for the product kernel. The value that we find is $\nu_y(\alpha=\frac{1}{2})=2.05$ for the product kernel, as expected (within the error of our methods).

For α close to 1, the ratios of the function $M_2(t)$ for the product kernel are very well behaved; these are shown in Fig. 8(a). For the range of α values shown in Fig. 8 one can combine the exponents for the functions $M_2(t)$ and $M_2(y)$ to obtain the relations

$$\Delta t\sim\Delta y^{1/\mu}\ , \tag{5.6}$$

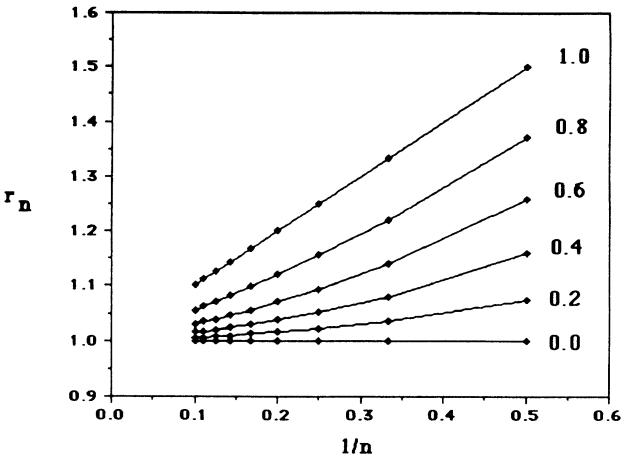


FIG. 7. Ratio plots r_n of (2.6) as a function of $1/n$ obtained from M_2 as a function of y for the sum kernel. The appropriate values of α are indicated on the graph. The curves for $\alpha=0$ and 1 correspond exactly to the cases $\nu_y=1$ and 2 [see Eqs. (5.3) and (5.4)].

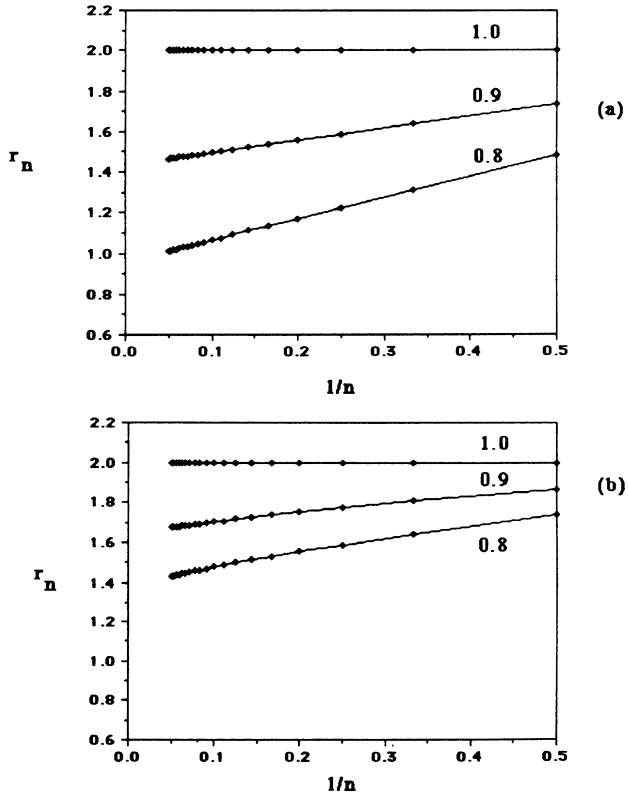


FIG. 8. (a) Ratio plots r_n of (2.6) as a function of $1/n$ obtained from $M_2(t)$ for the product kernel. The appropriate values of α are indicated on the graph. (b) A similar plot for $M_2(y)$. The curves for $\alpha=0$ and 1 both correspond exactly to the case $\nu_y=1$ [see Eqs. (5.3) and (5.5)].

$$\Delta y \sim \Delta t^{\mu} , \tag{5.7}$$

where

$$\mu = \nu_t / \nu_y . \tag{5.8}$$

Equations (5.6) and (5.7) relate the singular parts of the t and y dependences of M_2. Equation (5.6) is the analog of (2.5) for a finite value of t_g at the transition point. One has the following correspondence between the exponent γ of (2.5) and the exponent μ of (5.6):

$$\mu = -\gamma . \tag{5.9}$$

Using the exponents determined from the data of Fig. 8, the values of $1/\gamma$ obtained from (5.8) and (5.9) for $\alpha = 0.8$, 0.9, and 1.0 are shown in Fig. 6 [Padé approximants applied to $t = t(y)$ give the same results]. One sees that $1/\gamma \to -1$ as $\alpha \to 1$ and (5.6) gives the known result in that case, $t = y$. The solid line in Fig. 4(b) for the case of $\alpha = 0.9$ uses the value of $1/\gamma$ obtained from the data of Fig. 8; one sees that the ratios obtained from the function $t = t(y)$ are consistent with this slope.

In Fig. 6 one sees that we have been able to determine $1/\gamma(\alpha)$ first from the function $t = t(y)$ for values close to $\alpha = 0$ [using the data of Fig. 4(a)] and second from the functions $M_2(t)$ and $M_2(y)$ for values of α close to $\alpha = 1$ (using the data of Fig. 8). In between, we have not been able to determine the value of the exponent accurately, probably because the function is changing character from the behavior of (1.9) ($t \to \infty$ as $y \to y_g$) to that of (5.6) (t is finite as $y \to y_g$). In particular, we are not able to determine the value of $1/\gamma$ accurately at $\alpha = \frac{1}{2}$. Since we expect the behavior of the product kernel at $\alpha = \frac{1}{2}$ to be analogous to that of the sum kernel at $\alpha = 1$ and since for the latter one has $t = -\ln(1-y)$, corresponding formally to $1/\gamma = 0$, we expect that $1/\gamma$ will be zero for the product kernel at $\alpha = \frac{1}{2}$.

Figure 10 shows the ratios of the function $t = t(y)$ for the product kernel at $\alpha = \frac{1}{2}$. For comparison two special cases are shown. The first is the ratios for the function $-\ln(1-y)$, and the second is a line determined by the slope and intercept given by Padé approximant analysis ($y_g = 0.977$, $1/\gamma = 0.40$). One sees that the slope of the ratio points is similar to that of the $-\ln(1-y)$ curve, but that the intercepts for the two are not the same. The ratios do seem to be asymptotic to the curve determined by the Padé analysis, but the intercept is not exactly at $y_g = 1$. Thus while the ratios are extremely well behaved, we are not able to offer a definitive value of the exponent; indeed, part of the problem is that the functional form of t as a function of y in this transition region is probably not that given either by (2.5) or (5.6). Clearly, the function $(1-y) \sim \exp(-t/\tau)$ decays to zero too fast; we have also tried a stretched exponential

$$(1-y) \sim \exp[-(t/\tau)^{\beta}] ,$$

but the exponent β obtained form successive terms in the series (comparing actual coefficients with those predicted by the assumed functional form) do not approach a limit, but seem to extrapolate to zero, again indicating that the functional form is not exponential.

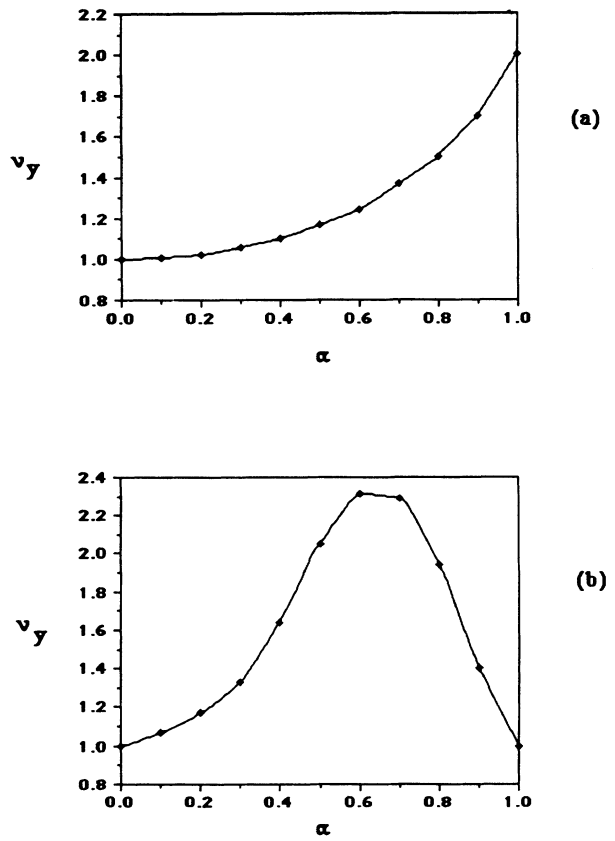


FIG. 9. Variation of the exponent ν_y [see (5.2)] as a function of α for (a) the sum kernel (obtained from the slopes of the ratio plots in Fig. 7) and (b) the product kernel (obtained from the slopes of the ratio plots in Fig. 8).

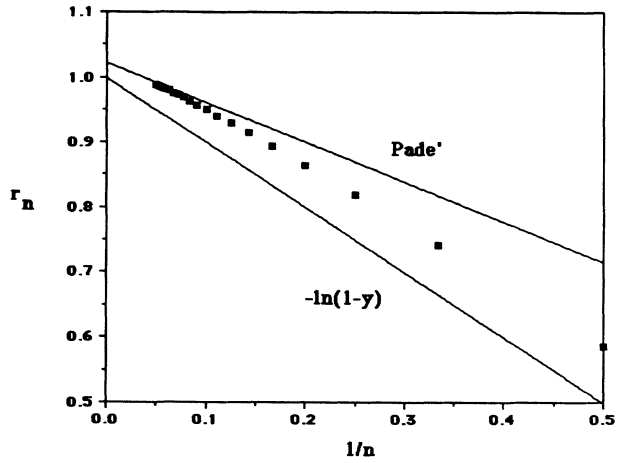


FIG. 10. Ratio plot for $t = t(y)$ for the product kernel for the case $\alpha = \frac{1}{2}$. The line marked $-\ln(1-y)$ is the result expected if $(1-y) \sim \exp(-t)$. The line marked Padé was constructed using the slope and intercept obtained from Padé approximants to the $t = t(y)$ series.

VI. OTHER KERNELS

The simple product kernel $K_{ij}=ij$ can be thought of as applying to the aggregation of two linear polymer chains, one with i sites for binding and the other with j sites for binding, hence $(i)\times(j)$ possible points at which the two can join. If one considers instead roughly spherical aggregates of i and j monomers reacting as in (1.1), then the rate of production of the product, $(i+j)$ is

$$\frac{dc_{i+j}}{dt}=kc_{ij} , \tag{6.1}$$

where c_{ij} is the density of i-j pairs of clusters close enough to react to give the merged product $(i+j)$. If we can use an equilibrium distribution of the i and j clusters in space (assuming diffusion is fast relative to the rate of the aggregation reaction so that the system is spatially always approximately in equilibrium), then we can estimate c_{ij} by using the pair distribution function $g_{ij}(r_{ij})$, where r_{ij} is the distance between the two clusters. One has

$$c_{ij}=\text{const}\times c_i c_j \int_{r_c}^{r_c+\Delta} g_{ij}(r_{ij})r^2 dr , \tag{6.2}$$

where r_c is the distance of closest approach of the two spheres and Δ is some small interval over which the two spheres can be considered close enough in order to react. Assuming a random distribution, we take $g_{ij}=1$ (at this point one could take into account excluded volume by using a more realistic, concentration-dependent form for g_{ij}; see Poland [22]) and we assume that Δ is very small, giving

$$c_{ij}\cong\text{const}'\times c_i c_j r_c(i,j)^2 , \tag{6.3}$$

where we have emphasized that r_c, the distance of closest approach of the two spheres, is a function of i and j, the number of monomers, respectively, in both spheres.

The volume of the sphere is proportional to the number of monomers in it. For a spherical cluster the radius is therefore proportional to $i^{1/3}$. One then has that

$$r_c(i,j)=\text{const}\times(i^{1/3}+j^{1/3}) . \tag{6.4}$$

Hence, from (6.3),

$$K_{ij}=k(i^{1/3}+j^{1/3})^2 , \tag{6.5}$$

where k is a constant independent of the size of the clusters. For clusters with minimal surface in d dimensions, the analog of (6.5) is

$$K_{ij}=k(i^{1/d}+j^{1/d})^{d-1} . \tag{6.6}$$

One sees that this form of kernel is a combination of the sum and product kernel that we have previously been using. The diagonal terms have the form $K_{ii}=i^{(d-1)/d}$; from our previous discussion, we expect that gelation at a finite time will only occur when $d\to\infty$ (i.e., there is no gelation in two or three dimensions).

Using the kernel of (6.6) in two (2D) and three (3D) dimensions, one obtains the ratios for the function $t=t(y)$, as shown in Fig. 11. Again, the ratios are very well behaved and point to $y_g=1$, indicating that there is no gelation at a finite time. The slopes give the following estimates of the exponents γ for these two cases:

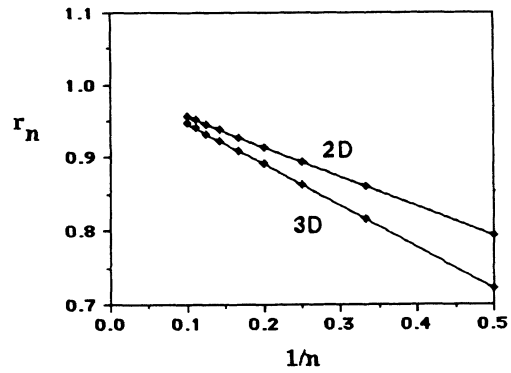


FIG. 11. Ratio plots r_n of (2.6) as a function of $1/n$ obtained from $t=t(y)$ for the kernel of (6.6) for two and three dimensions.

$$1/\gamma=\begin{cases}0.588 & (2D)\\ 0.441 & (3D)\end{cases} \tag{6.7}$$

and

$$M_0(t)\sim\begin{cases}t^{-1.70} & (2D)\\ t^{-2.27} & (3D) .\end{cases} \tag{6.8}$$

As we have seen, the series can be used to estimate the asymptotic form quite accurately. But they can also be used to construct the function over the whole time range. As an example, we take the kernel just discussed for the case of three dimensions. It is convenient to introduce the following Euler transform of time which maps the interval $t=0$ to ∞ onto the unit line

$$s=t/(1+t),\quad t=s/(1-s) . \tag{6.9}$$

With this variable we have

$$M_0\sim(1-s)^\gamma \tag{6.10}$$

or

$$M=M_0{}^{1/\gamma}\sim(1-s) . \tag{6.11}$$

The advantage of the latter form is that M goes to zero linearly with s. From the power series in time, we can construct the s series for M exactly, say, through N terms. Since M goes to zero linear in s, we can simply add on an $(N+1)$th-order term in s to force M to go to zero at $s=1$ (it should be a very small correction, reflecting the error arising from truncation of the series). In this manner we obtain

$$\begin{aligned}M_0(s)=[&1-0.441s-0.245s^2-0.136s^3-0.076s^4\\ &-0.042s^5-0.023s^6-0.012s^7-0.006s^8\\ &-0.003s^9-0.001s^{10}-0.015s^{11}]^{2.27} .\end{aligned} \tag{6.12}$$

This function is plotted in Fig. 12 (solid points) and compared with the simple function (solid line)

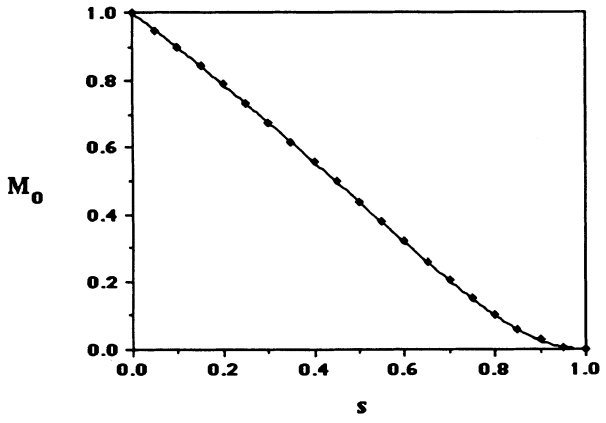


FIG. 12. The behavior of $M_0(s)$ for the irreversible aggregation of spherical clusters $[s=t/(1+t)]$. The solid points are obtained using the truncated series of (6.12), while the solid curve is the function of (6.13).

$$M_0=\left[\frac{1}{1+\frac{1}{\gamma}t}\right]^{\gamma}=\left[\frac{1}{1+0.441s/(1-s)}\right]^{2.27}. \tag{6.13}$$

The relation of (6.13) reproduces the results of (6.12) to almost three significant figures over the whole range of s.

VII. DISCUSSION

We have shown that power series in time can yield accurate information about the asymptotic behavior of aggregation processes. In particular, the inversion of the time series for the first moment of the cluster distribution, M_0, to give time as a function of the variable $y=1-M_0$ in all cases gives a smoothly varying series with well-behaved ratios.

Assuming an asymptotic power-law form $M_0\sim t^{-\gamma}$, we are able to determine the exponent γ numerically (see Fig. 3) for the sum kernel for α in the range 0 to 1. Leyvraz [23] has given the relation

$$1/\gamma=(1-\alpha)/(1-\alpha/2)$$

for the sum kernel of (1.6), based on an assumed asymptotic form for the cluster probabilities. At $\alpha=\frac{1}{2}$ this gives $1/\gamma=\frac{2}{3}$, which is somewhat higher than the value of $1/\gamma=0.57$ that we find [see (3.7)].

For the product kernel we clearly detect the gelation transition for $\alpha>\frac{1}{2}$. As discussed earlier, we can only determine the exponent γ with any confidence near the end points, $\alpha=0$ and 1. Presumably, the functional form in the midrange of α is more complicated than a simple power law or it is only very slowly asymptotic to a power law. The series $t=t(y)$ for the case of $\alpha=\frac{1}{2}$ for the product kernel is, however, very smooth, as indicated by the ratios shown in Fig. 10. It remains a challenge to extract the true nature of the functional form for this relaxation process from these data.

[1] M. von Smoluchowski, Z. Phys. Chem. **92**, 129 (1918).
[2] J. B. McLeod, Quart. J. Math. **13**, 119 (1962); **13**, 193 (1962); **13**, 283 (1962).
[3] P. G. J. van Dongen, J. Phys. A **20**, 1889 (1987).
[4] W. H. White, Proc. Am. Math. Soc. **80**, 273 (1980).
[5] F. Leyvraz and H. R. Tschudi, J. Phys. A **15**, 1951 (1982).
[6] F. Leyvraz and H. R. Tschudi, J. Phys. A **14**, 3389 (1981).
[7] F. Leyvraz, J. Phys. A **16**, 2861 (1983).
[8] R. M. Ziff, J. Stat. Phys. **23**, 241 (1980).
[9] E. Buffet and R. F. Werner, J. Math. Phys. **32**, 2276 (1991).
[10] P. G. J. van Dongen and M. H. Ernst, J. Phys. A **16**, L327 (1983).
[11] N. J. Kokholm, J. Phys. A **21**, 839 (1988).
[12] B. Lu, J. Stat. Phys. **49**, 669 (1987).
[13] R. P. Treat, J. Phys. A **23**, 3003 (1990).
[14] Y. Jiang and H. Gang, Phys. Rev. B **40**, 661 (1989).
[15] Y. Jiang, H. Gang, and M. BenKun, Phys. Rev. B **41**, 9424 (1990).
[16] P. L. Karpivsky, J. Phys. A **24**, 4697 (1991).
[17] D. Poland, J. Comp. Chem. **11**, 382 (1990).
[18] S. Song and D. Poland, J. Phys. A **25**, 3913 (1992).
[19] D. Poland, J. Phys. A **24**, 229 (1991).
[20] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).
[21] R. M. Ziff, M. H. Ernst, and E. M. Hendriks, J. Phys. A **16**, 2293 (1983).
[22] D. Poland, J. Chem. Phys. **97**, 470 (1992).
[23] F. Leyvraz, Phys. Rev. A **29**, 854 (1984).