

# Aggregation Beyond the Gel Point: A New Class of Exactly Solvable Models

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Received February 19, 1996

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The existing models describing the kinetics of aggregation in the presence of an infinite cluster, or *gel*, are reviewed, and a new class of post-gel models is proposed. In this new class of models, clusters are assumed to be acyclic and the rate constant for reactions involving the gel can be varied. The model is called the *generalized acyclic model* (GAM) since it generalizes Stockmayer's model and Ziff's third model. It is shown that the GAM can be solved exactly in terms of standard (hypergeometric) functions. The solutions are analyzed in detail, both asymptotically in various limits and numerically.

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**KEY WORDS:** Aggregation; gelation; Smoluchowski's equation;  $RA_j$ -model.

## 1. INTRODUCTION

There exists a close relationship between the *kinetic* and *equilibrium* theories of polymerization. The kinetic theory of polymerization was founded in 1916 by Smoluchowski,<sup>(1, 2)</sup> who wrote down an infinite set of coupled chemical rate equations for the concentrations  $c_k(t)$  of polymers of size  $k$  (or  $k$ -mers) at time  $t$ :

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \quad (1)$$

Here  $K_{ij}$  is the rate constant for reactions between clusters of size  $i$  and size  $j$ . If the initial state consists only of monomers, the appropriate starting point for the solution of (1) is the so-called *monodisperse* initial condition,  $c_k(0) = M(0) \delta_{k1}$ . One of the reasons why Smoluchowski's equation is of

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Dedicated to Matthieu Ernst, on the occasion of his 60th birthday.

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interest in physics is the possible occurrence of a nonequilibrium phase transition. This transition is characterized by the formation of an infinite cluster (or *gel*) after a finite time  $t_c$ . Until such a gelation transition occurs, Smoluchowski's equation conserves the total concentration of monomeric units,  $M(t) \equiv \sum_k k c_k(t) = M(0)$ . The concentration of monomeric units will be normalized to unity below,  $M(0) = 1$ , which can be achieved by an appropriate choice of the unit of volume. The kinetic equation (1) allows for several exactly solvable models. A first example, corresponding to  $K_{ij} = 1$  and the monodisperse initial condition, was given already by Smoluchowski. Several other exactly solvable models have since been found, all of which have the bilinear form  $K_{ij} = A + B(i + j) + Cij$ . Apart from the knowledge gained from these exactly solvable models, much is known about the structure of the solution of Smoluchowski's equation for large classes of rate constants in various limits. Examples are the long-time limit,<sup>(3)</sup> the limit of large cluster sizes,<sup>(4)</sup> and, most importantly, the scaling limit.<sup>(5)</sup>

On the other hand, the equilibrium theory of polymerization traditionally employs combinatorial methods.<sup>(6,7)</sup> A typical example is the so-called  $RA_f$ -model, in which monomers carry  $f$  identical (but distinguishable) reactive groups. The monomers can react with one another and form larger clusters. In the  $RA_f$ -model it is assumed that reactions are possible only between reactive groups on different clusters, so that loops do not occur. This implies that  $k$ -mers are branched structures having  $k - 1$  bonds and  $\sigma_k(f) \equiv (f - 2)k + 2$  unreacted reactive groups. All reactive groups are assumed to be *a priori* equally reactive. The equilibrium size distribution can then be determined by the standard methods of statistical mechanics, i.e., by writing down the entropy functional and calculating the most probable distribution. The result can conveniently be formulated in terms of the *extent of reaction*  $\alpha$  of the system, which is defined as the fraction of all reactive groups that have actually reacted. One finds that the concentration  $\bar{c}_k(\alpha)$  of clusters of size  $k$  takes the form

$$\bar{c}_k(\alpha) = A(\alpha) \mathcal{N}_k \xi(\alpha)^k \quad (2)$$

where  $A(\alpha) = f(1 - \alpha)^2/\alpha$ ,  $\xi(\alpha) = \alpha(1 - \alpha)^{f-2}/f$ , and  $\mathcal{N}_k$  satisfies the recursion relation

$$(k - 1) \mathcal{N}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} \mathcal{N}_i \mathcal{N}_j \quad (3)$$

which is to be solved subject to  $\mathcal{N}_1 = 1$ . The constants  $\mathcal{N}_k$  represent the number of different  $k$ -mer configurations. Their explicit form is  $\mathcal{N}_k = f^k [ (f - 1)k ]! / [ \sigma_k(f)! k! ]$ .

The close connection between the kinetic and equilibrium theories of polymerization was first addressed by Stockmayer<sup>(7)</sup> and then, in more detail, by Ziff<sup>(8)</sup> and Ziff and Stell.<sup>(9)</sup> These authors pointed out that the equilibrium size distribution  $\bar{c}_k(\alpha)$  found above for the  $RA_f$ -model, also provides the exact solution for Smoluchowski's equation (1) with rate constants  $K_{ij} = \sigma_i(f) \sigma_j(f)$  and monodisperse initial conditions, if one supplies the extent of reaction  $\alpha$  with the appropriate time dependence. Insertion of (2) into (1) yields  $\dot{\alpha} = f(1 - \alpha)^2$ , so that the solution of Smoluchowski's equation for the  $RA_f$ -model is given by  $c_k(t) = \bar{c}_k(\alpha(t))$ , with  $\alpha(t) = ft/(1 + ft)$ .

An interesting complication occurs as the extent of reaction increases from  $\alpha = 0$  to a critical value  $\alpha_c = (f - 1)^{-1}$ . At  $\alpha_c$  one observes that the average cluster size diverges:

$$\langle k \rangle = M_2(\alpha) \equiv \sum_{k=1}^{\infty} k^2 \bar{c}_k(\alpha) = \frac{1 + \alpha}{1 - (f - 1)\alpha} \rightarrow \infty \quad (\alpha \uparrow \alpha_c) \quad (4)$$

The same divergence obviously occurs in the kinetic theory of polymerization for  $t \uparrow t_c$ , where  $t_c$  is defined by  $\alpha(t_c) \equiv \alpha_c$ . The interpretation of the divergence is wellknown: at  $\alpha_c$  an infinite cluster, or *gel*, is formed. Since the  $RA_f$ -model, as it stands, contains assumptions concerning finite-size clusters only, one has to supplement it with a description of the infinite cluster in order to make definite statements about the post-gel stage. Clearly an infinity of gelmodels is possible in principle. Two models for the post-gel stage (proposed by Flory and by Stockmayer, respectively) are exactly soluble and very wellknown. I briefly review their properties below. A third post-gel model has been proposed by Ziff<sup>(8)</sup> and Ziff and Stell.<sup>(9)</sup> The exact solution of this third model is, to the best of my knowledge, as yet unknown. In addition, I will present a new class of models which generalize Stockmayer's and Ziff's models and preserve the restriction that loops do not occur. This new class will be referred to as the *generalized acyclic model* (GAM). The main point of this paper is to show that both the third model and the GAM can be solved exactly in terms of standard functions. The properties of the exact solution will be discussed in detail.

This paper is organized as follows. First, in Section 2, I review the post-gel models proposed by Flory, Stockmayer, and Ziff and introduce the new GAM. The exact solution of the GAM (and hence also of the third model) is presented in Section 3. The properties of the solution are studied in various limits. A summary of the results and a discussion are given in Section 4.

## 2. MODELS FOR THE POST-GEL STAGE

Different post-gel models are characterized by different assumptions concerning the allowed reactions between the finite-size clusters (the sol) and the infinite cluster (or gel) and also by different assumptions concerning reactions within the gel. In this paper attention is restricted to post-gel versions of the  $RA_f$ -model. Accordingly all post-gel models to be discussed below correspond to modifications of Smoluchowski's equation of the form

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j - \sigma_k(f) c_k X(t) \quad (5)$$

where  $K_{ij} = \sigma_i(f) \sigma_j(f)$  and  $X(t)$  represents the properties of the gel. Physically, one expects that  $X(t)$  will be proportional to the concentration  $[A_g^f]$  of free reactive groups in the gel. Then, the kinetic equation (5) is to be supplemented with a constitutive equation for  $[A_g^f]$  in the various post-gel models. However, independent of the detailed form of  $[A_g^f]$ , one can already conclude from the linear  $k$ -dependence of  $\sigma_k(f)$  in (5) that the size distribution  $c_k(t) = \bar{c}_k(\alpha)$  can be cast into the form

$$\bar{c}_k(\alpha) = M \bar{c}_k(\alpha_s) \quad (6)$$

where  $\bar{c}_k(\alpha_s)$  is given by (2) and  $0 \leq \alpha_s \leq \alpha_c$ . This observation was made also by Ziff.<sup>(8)</sup> Physically, the form (6) simply states that the post-gel distribution of solclusters can be characterized by an extent of reaction  $\alpha_s$  and that the sol mass is given by  $\sum_k k \bar{c}_k(\alpha) = M$ , where  $M$  is strictly less than unity for  $\alpha > \alpha_c$ . The dependence of  $\alpha_s$  and  $M$  upon time (or upon  $\alpha$ ) is of course different in different post-gel models.

In the simplest possible post-gel model, which was proposed by Flory, it is assumed that the pre-gel distribution (2), with  $\alpha > \alpha_c$ , is valid also in the post-gel stage. This fixes  $X(t)$  in (5). The time dependence of  $\alpha(t)$  is given by the same equation  $\dot{\alpha} = f(1 - \alpha)^2$ , or  $\alpha(t) = ft/(1 + ft)$ , as for  $\alpha < \alpha_c$ . Comparison of (2) and (6) shows that the extent of reaction  $\alpha_s(\alpha)$  in the sol is given by the smallest positive real root of  $\zeta(\alpha_s) = \zeta(\alpha)$ . Thus  $\alpha_s(t)$  is known, since  $\alpha(t)$  is known. Note the hierarchy  $0 < \alpha_s < \alpha_c < \alpha < 1$ . The sol mass in Flory's model follows as  $M = A(\alpha)/A(\alpha_s) < 1$ . The *interpretation* of Flory's post-gel model is already clear from the chemical rate equation  $\dot{\alpha} = f(1 - \alpha)^2$ , which implies that any pair of reactive groups in the system is allowed to react. Since this implies in particular that any pair of reactive groups on the (macroscopically large) gelcluster may react, it is clear that the gel in Flory's model cannot be acyclic.<sup>2</sup>

<sup>2</sup> Note, however, that the *sol*-clusters in Flory's model are acyclic, since the rate of loop formation in finite-size clusters is inversely proportional to the system size. This rate therefore vanishes in the thermodynamic limit.

The latter point, that the gel in Flory's model contains loops, has been criticized by Stockmayer, who pointed out that the occurrence of loops violates one of the basic assumptions underlying the derivation of the size distribution. Instead, Stockmayer proposed a different solution, in which the gel is acyclic. In addition, the extent of reaction in the sol is assumed to be pinned at its critical value,  $\alpha_s = \alpha_c$ . The standard interpretation of Stockmayer's solution in terms of the kinetic model (5) is that the gel is *inactive*.<sup>3</sup> This follows by insertion of the Ansatz (6) into (5), since a consistent solution requires that the reactivity of the gel vanishes:  $X(t) = 0$ . It is clear that the absence of sol-gel reactions makes Stockmayer's additional assumption, that the gel be acyclic, redundant. In this sense Stockmayer's model provides a description for the sol only.

In addition to the Flory- and Stockmayer-type post-gel models, a third model has been proposed by Ziff<sup>(8)</sup> and Ziff and Stell.<sup>(9)</sup> The basic idea of the third model is that the gel is acyclic, as assumed by Stockmayer, but that (in contrast to Stockmayer's model) sol-gel reactions are allowed. This model treats sol-sol and sol-gel reactions in a *symmetric* manner, in that both types of reactions have the same rate constant:  $X(t) = [A_g^f]$ . Physically, it would be of interest to tone down this restriction. Various mechanisms, such as steric hindrance or a lower diffusion rate of the gel, might cause the effective sol-gel rate constant to differ from the rate constant for reactions between finite clusters. To incorporate this effect I propose a new class of models, in which the acyclic nature of all clusters is retained, but the reaction rates for sol-sol and sol-gel reactions may differ. This corresponds to  $X(t) = \kappa [A_g^f]$  in (5), with an arbitrary nonnegative rate constant  $\kappa$ . This new class of models includes the third model ( $\kappa = 1$ ) and Stockmayer's model ( $\kappa = 0$ ) as special cases. Below I will refer to the new class of models as the *generalized acyclic model*, or GAM.

For all models of GAM type, the condition, that the gel be acyclic, implies that  $[A_g^f] = (f - 2)(1 - M)$  in (5) or, equivalently, that the extent of reaction in the gel is  $\alpha_g = 2/f$ . The extent of reaction in the sol follows as

$$\alpha_s = \sum_{k=1}^{\infty} 2(k-1) c_k \bigg/ \sum_{k=1}^{\infty} f k c_k = \frac{2}{f} \left( 1 - \frac{M_0}{M} \right) \quad (7)$$

<sup>3</sup> This is the *standard*,<sup>(8,9)</sup> but not the *only* possible interpretation of Stockmayer's model. Stockmayer's assumption  $\alpha_s = \alpha_c$  is also compatible with a sol-gel interaction of the form  $-\bar{\sigma} c_k X(t)$ , where  $\bar{\sigma}$  is  $k$ -independent. This alternative interpretation, although perhaps interesting at a more abstract level, has no combinatorial meaning in the  $RA_f$ -model, where  $\bar{\sigma} = \sigma_k(f) = (f - 2)k + 2$  represents the number of free A-groups on a  $k$ -mer.

where  $M_0 = \sum_k c_k(t)$  represents the total concentration of finite-size clusters. This in turn implies that the total extent of reaction is given by  $\alpha = M\alpha_s + (1 - M)\alpha_g = 2(1 - M_0)/f$ , which may be inverted to yield  $M_0 = 1 - f\alpha/2$ . Insertion into (7) leads to a first relation between the three variables  $M$ ,  $\alpha_s$ , and  $\alpha$ :

$$M = \left(1 - \frac{f}{2}\alpha\right) / \left(1 - \frac{f}{2}\alpha_s\right) \quad (8)$$

A *second* relation between  $M$ ,  $\alpha_s$ , and  $\alpha$  will be constructed below by imposing that the post-gel size distribution (6) satisfies Smoluchowski's equation (5). As a result of these two relations, only one of the variables  $M$ ,  $\alpha_s$ , and  $\alpha$  can be considered independent.

### 3. EXACT SOLUTION OF THE GENERALIZED ACYCLIC MODEL

In order to obtain a functional relation between the as-yet-independent variables  $\alpha_s$  and  $M$ , I first derive two coupled equations for the time evolution of  $\alpha(t)$  and  $M(t)$ . The starting point is the kinetic equation for the GAM, which is given by (5) with  $X(t) = \kappa[A_g^F]$  and  $\kappa \geq 0$ . The rate equation for the extent of reaction  $\alpha$  follows from combination of (5) and the relation  $\alpha = 2(1 - M_0)/f$ . One finds

$$\begin{aligned} \dot{\alpha} &= -\frac{2}{f}\dot{M}_0 = \frac{1}{f}[A_s^F]^2 + \frac{2\kappa}{f}[A_s^F][A_g^F] \\ &= M(1 - \alpha_s)[fM(1 - \alpha_s) + 2\kappa(f - 2)(1 - M)] \end{aligned} \quad (9a)$$

where  $[A_g^F] = (f - 2)(1 - M)$  has been used and  $[A_s^F]$  follows from

$$[A_s^F] = \sum_{k=1}^{\infty} \sigma_k \bar{c}_k(\alpha) = M \sum_{k=1}^{\infty} \sigma_k \bar{c}_k(\alpha_s) = fM(1 - \alpha_s)$$

Note that  $\alpha$  in (9a) is now known as a function of  $\alpha_s$  and  $M$  only. Similarly the time dependence of the sol mass  $M(t)$  can be determined by multiplication of (5) with  $k$  and summation over all  $k$ . The result is

$$\begin{aligned} \dot{M} &= -\kappa[A_g^F] M[(f - 2)M_2(\alpha_s) + 2] \\ &= -\kappa f(f - 2) M(1 - M) A(\alpha_s) \end{aligned} \quad (9b)$$

where  $A(u) \equiv (1 - u)/[1 - (f - 1)u]$ . In the derivation of (9b) the explicit form of  $M_2(\alpha_s)$  in (4) and that of  $[A_g^F]$  have been used. For the third

model ( $\kappa = 1$ ), the coupled equations (9) are equivalent to Eqs. (C10) and (C11) in ref. 9. Below it is shown how these equations can be solved exactly for all  $\kappa \geq 0$ .

The method of solution to be presented below contains two steps. As a first step it appears to be convenient to eliminate the time variable and derive a differential equation for  $\alpha_s(M)$ . The differential equation for  $\alpha_s(M)$  can then be solved after a few suitable transformations. Once  $\alpha_s(M)$  is known, one can (as a second step) reintroduce the original time variable and calculate  $M(t)$  from (9b) by separation of variables. The fact that the GAM becomes soluble if formulated in terms of the extent of reaction once more reflects the close relationship between the kinetic and equilibrium theories of polymerization.

I start with the first step, the derivation of a differential equation for  $\alpha_s(M)$ . The easiest way to do this is to note that  $\dot{\alpha}$  can be rewritten as  $\dot{\alpha} = \dot{M}(\alpha_s - 2/f + M d\alpha_s/dM)$  on account of (8). Division of (9a) by (9b) thus leads to a relation between  $\alpha_s$ ,  $M$ , and  $d\alpha_s/dM$ . This relation can be rewritten as a first-order nonlinear differential equation for  $\alpha_s(M)$ :

$$\frac{d\alpha_s}{dM} = \frac{(f-2)\alpha_s}{fM} - \frac{(1-\alpha_s)[1-(f-1)\alpha_s]}{\kappa(f-2)(1-M)} \tag{10}$$

The structure of this result is already much simpler than the starting point (9). Note that (10) is an equation of Riccati type. The initial condition  $\alpha_s(1) = \alpha_c = (f-1)^{-1}$  also fixes the value of the derivative at  $\alpha = \alpha_c$  as

$$(d\alpha_s/dM)_c = (f-2)\kappa/[f(f-1)(1+\kappa)]$$

This result differs in general (i.e., for  $\kappa \neq 1$ ) from the behavior found in Flory's model, which has

$$(d\alpha_s/dM)_c = (f-2)/[2f(f-1)]$$

For future reference, I also note that the large-time behavior of  $\alpha_s(M)$ , which corresponds to  $M \downarrow 0$ , follows from (10) as

$$\alpha_s(M) \sim CM^{1-2/f} - \frac{fM}{2\kappa(f-2)} + \dots \quad (M \downarrow 0; \kappa > 0) \tag{11}$$

where the integration constant  $C$  remains as yet undetermined. This can be compared to Flory's model, which has  $\alpha_s \sim M^{1-2/f}$ , so that  $C^{\text{Flory}} = 1$  for all  $f > 2$ .

### 3.1. Solution in Several Special Limits

Before addressing the general solution of (10), I consider several relatively simple limits. First, in the limit  $\kappa \downarrow 0$  one expects  $\alpha_s \rightarrow \alpha_c$ , which is the solution of Stockmayer's model. Indeed one finds that (10) allows for a solution of the form

$$\alpha_s \sim \alpha_c \left[ 1 - \frac{\kappa}{fM} (f-2)(1-M) \right] + \mathcal{O}(\kappa^2) \quad (\kappa \downarrow 0) \quad (12)$$

Second, in the limit  $\kappa \rightarrow \infty$ , Eq. (10) allows for a simple solution, namely

$$\alpha_s \sim \alpha_c M^{1-2/f} \quad (\kappa \rightarrow \infty) \quad (13)$$

Clearly, the aggregation process in the post-gel stage will take place on a very fast time scale, of order  $1/\kappa$ , in this limit. Third, one finds relatively simple expressions for the rescaled extent of reaction  $\tilde{\alpha}_s \equiv f\alpha_s$  in the high-functionality limit ( $f \rightarrow \infty$ ). The result for general  $\kappa > 0$  is given by

$$\tilde{\alpha}_s(M) = MF \left( \frac{1}{\kappa}, 1; 1 + \frac{1}{\kappa}; 1 - M \right) \quad (f = \infty) \quad (14)$$

where  $F(a, b; c; x)$  denotes a hypergeometric function; see ref. 10. For the particular parameter values in (14), the hypergeometric function is essentially an incomplete beta function; see Eq. (6.6.8) of ref. 10. A simpler result is obtained for the third model ( $\kappa = 1$ ), since in this case (14) reduces to  $\tilde{\alpha}_s(M) = M \ln(M^{-1})/(1-M)$ . This result coincides with that found for Flory's model, since loops are unimportant in the limit  $f \rightarrow \infty$ .

### 3.2. Solution of the General Model

Next I proceed and solve the general equation (10) for the GAM by means of a few suitable transformations; As a first step it is convenient to transform from  $\alpha_s$  to a new variable  $y = A(\alpha_s) - 1$ , where  $A(u) = (1-u)/[1-(f-1)u]$  has been introduced below (9b). Note that  $A$  is its own inverse,  $A^2 = 1$ , so that reversely  $\alpha_s = A(y+1)$ . The transformation  $y = A(\alpha_s) - 1$  is motivated by the asymptotic behavior of  $\alpha_s$  for  $M \uparrow 1$  and  $M \downarrow 0$ , since it maps the interval  $0 < \alpha_s < \alpha_c$  onto the positive real axis: one finds that

$$y(M) \sim f(1+\kappa)/[(f-1)\kappa(1-M)] \rightarrow \infty \quad \text{as} \quad M \uparrow 1$$



while  $y(M) \downarrow 0$  for  $M \downarrow 0$ . The function  $y(M)$  satisfies another Riccati equation,

$$\frac{dy}{dM} = \frac{f-1}{fM} y^2 + \left[ \frac{f-2}{fM} - \frac{1}{\kappa(1-M)} \right] y - \frac{1}{\kappa(1-M)}$$

This first-order *nonlinear* differential equation can be transformed to a second-order *linear* differential equation by means of the substitution  $y(M) = -fM(f-1)^{-1} z'(M)/z(M)$ . The result is

$$M(1-M) z'' + \left[ \frac{2}{f} + \left( \frac{1}{\kappa} - \frac{2}{f} \right) M \right] z' - \frac{f-1}{f\kappa} z = 0$$

This is a special case of the hypergeometric differential equation. In the notation of ref. 10, Chapter 15, the parameters  $(a, b, c)$  in the differential equation are determined by  $a + b = -[(f-2)/f + 1/\kappa]$ ,  $ab = (f-1)/f\kappa$ , and  $c = 2/f$ . If desired,  $a$  and  $b$  can easily be calculated explicitly. According to ref. 10, Eqs. (15.5.5) and (15.5.6), the hypergeometric differential equation has two independent solutions,  $w_{1(1)}(M)$  and  $w_{2(1)}(M)$ , which have different critical behavior:  $w_{1(1)} \sim 1$  and  $w_{2(1)} \sim (1-M)^{1+1/\kappa}$  for  $M \uparrow 1$ . I now impose the initial value  $(d\alpha_s/dM)_c = (f-2)\kappa/[f(f-1)(1+\kappa)]$  and find that the physical solution is given by  $w_{2(1)}(M)$ , so that

$$z(M) = (1-M)^{1+1/\kappa} F\left(1 + \frac{1}{\kappa} + a, 1 + \frac{1}{\kappa} + b; 2 + \frac{1}{\kappa}; 1-M\right) \quad (15)$$

This yields for the function  $y(M)$  on account of Eq. (15.2.1) of ref. 10

$$y(M) = \frac{fM(1+\kappa)}{(f-1)(1-M)\kappa} + \frac{M(f+1+2\kappa) F(2+1/\kappa+a, 2+1/\kappa+b; 3+1/\kappa; 1-M)}{(f-1)(1+2\kappa) F(1+1/\kappa+a, 1+1/\kappa+b; 2+1/\kappa; 1-M)} \quad (16)$$

The explicit  $M$ -dependence of  $\alpha_s(M)$  and  $\alpha(M)$  now follows from  $\alpha_s(M) = A(y+1)$  and relation (8), respectively. This concludes the first step in the solution of Eq. (9).

The second step in the solution of (9) has now become simple. Since  $\alpha_s(M)$  is explicitly known, the calculation of  $M(t)$  in (9b) for  $t > t_c = 1/f(f-2)$  has been reduced to a single quadrature, namely

$$\int_M^1 \frac{dx}{x(1-x)[y(x)+1]} = \kappa(t-t_c)/t_c \equiv \tau(t) \quad (17)$$

with  $y(M)$  given by (16). For  $\kappa = 0$ , insertion of Eq. (12) into (17) yields the well-known result for the sol mass in Stockmayer's model,  $M(t) = [1 + b_1(t - t_c)/t_c]^{-1}$  with  $b_1 = f/(f - 1)$ . For all  $\kappa > 0$ , it is convenient to introduce a *rescaled* time variable  $\tau(t) = \kappa(t - t_c)/t_c$ . At large times ( $\tau \gg 1$ ) one then finds that the sol mass decreases exponentially,  $M(t) \sim Z(\kappa) e^{-\tau(t)}$ , where the prefactor  $Z(\kappa) > 0$  is explicitly known in terms of a finite integral.

### 3.3. Various Limits and Numerical Results

Consider the general solution  $\alpha_s(M) = A(y + 1)$ , with  $y = y(M)$  determined by (16). The exact solution should obviously agree with the asymptotic results (12)–(14) obtained in the limits  $\kappa \downarrow 0$ ,  $\kappa \rightarrow \infty$ , and  $f \rightarrow \infty$ . I checked that this is indeed the case by expanding (15) in powers of  $\kappa$ ,  $1/\kappa$ , and  $1/f$ , respectively. Another limit of interest is  $M \downarrow 0$ , which is relevant at large times. This limit will be discussed in more detail.

The behavior of  $\alpha_s(M)$  for  $M \downarrow 0$  follows from the asymptotic behavior of (15), which can be determined from the linear transformation formula (15.3.6) of ref. 10 for hypergeometric functions. One finds full agreement with (11), including the subdominant term. In addition, one finds an explicit expression for the constant  $C$ , which remained undetermined in (11), namely

$$C = -\frac{B(-(f - 2)/f, 2(f - 1)/f + 1/\kappa + b)}{(f - 1) B(1 + 1/\kappa + a, (f - 2)/f)}$$

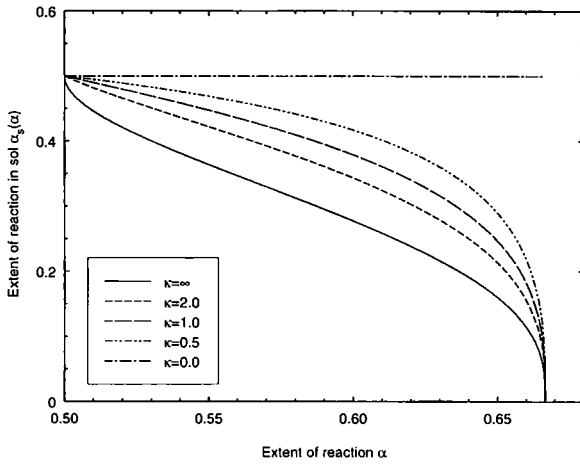
where  $B(x, y)$  is the beta function. An interesting special case occurs in the high-functionality limit ( $f \rightarrow \infty$ ). In this case one finds that

$$C = \frac{1}{2\kappa} \left( 1 + \frac{2}{f} \right) + \frac{1}{f\kappa} \left[ \psi(1) - \psi\left(\frac{1}{\kappa}\right) \right] + \mathcal{O}\left(\frac{1}{f^2}\right) \quad (f \rightarrow \infty)$$

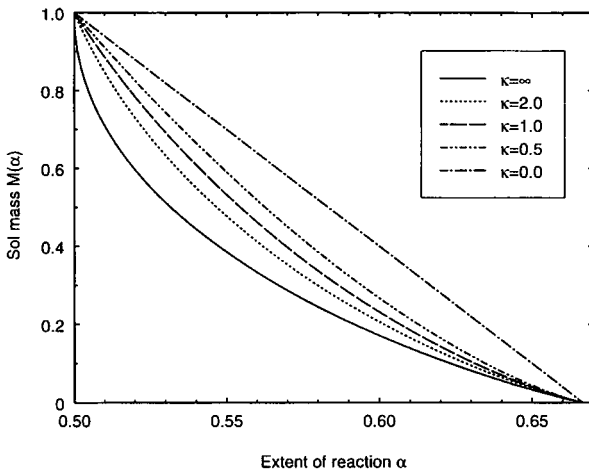
where  $\psi(x)$  is the digamma function<sup>(10)</sup> and  $\psi(1)$  is related to Euler's constant:  $\psi(1) = -\gamma$ . Insertion of  $C$  into (11) and inspection of the result shows that the limits  $M \downarrow 0$  and  $f \rightarrow \infty$  do not commute. If one takes the limit  $f \rightarrow \infty$  first and then  $M \downarrow 0$ , one obtains

$$\tilde{\alpha}_s(M) \sim \frac{M}{\kappa} \left[ \ln(M^{-1}) + \psi(1) - \psi\left(\frac{1}{\kappa}\right) \right]$$

On the other hand, if one takes the limit  $M \downarrow 0$  first and then  $f \rightarrow \infty$ , one finds that  $\tilde{\alpha}_s(M) \sim CM$ , with a divergent prefactor  $C \sim f/2\kappa$ . The conclusion is that, in order to obtain the correct small- $M$  behavior for all  $f$ ,



(a)



(b)

Fig. 1. (a) The extent of reaction in the sol  $\alpha_s$ , and (b) the sol mass  $M$ , both as a function of the total extent of reaction  $\alpha$ , for  $f = 3$  and various values of the sol-gel rate constant:  $\kappa = 0.0, 0.5, 1.0, 2.0, \infty$ .

including  $f \rightarrow \infty$ , one has to take also the subleading term in the small- $M$  expansion into account.

Next I present a graphical analysis of the results derived above. For reasons of uniformity, I focus on trifunctional units ( $f=3$ ). In Fig. 1, results are presented for the extent of reaction in the sol ( $\alpha_s$ ) and the sol mass ( $M$ ) as a function of the total extent of reaction  $\alpha$ , for various values of the rate constant  $\kappa$ . It is seen that both  $\alpha_s$  and  $M$  steadily decrease as a function of  $\kappa$ , approaching a *finite* limit as  $\kappa \rightarrow \infty$ . Note that  $\alpha_c = 1/2 < \alpha < \alpha_x = 2/3$  for  $f=3$ . Second, to study the time dependence of  $\alpha(t)$ , I calculated  $M(t)$  from (17) and inserted the result into  $\alpha(M)$ . For  $\kappa=0$  one finds a simple explicit result:  $\alpha = 2[1 - b_2 M(t)]/f$ , with  $b_2 = (f-2)/(2(f-1))$  and  $M(t)$  as calculated below (17). For various values of  $\kappa > 0$  the extent of reaction  $\alpha$  is sketched in Fig. 2 as a function of the rescaled time variable  $\tau(t) = \kappa(t - t_c)/t_c$ . One finds that  $\alpha(\tau)$  steadily decreases as  $\kappa$  increases. At fixed  $\kappa$  the extent of reaction approaches the asymptote  $\alpha = 2/f$  exponentially fast as a function of time:  $(2/f - \alpha) \sim 2Z(\kappa) e^{-\tau}/f$  for  $\tau \rightarrow \infty$ . The prefactor  $Z(\kappa)$  of the exponential time dependence can be determined numerically. For  $\kappa = 0.5, 1.0, 2.0$ , and  $\infty$ , one finds  $Z(\kappa) \sim 0.0523, 0.0874, 0.1309$ , and  $0.2530$ , respectively. For  $\kappa \downarrow 0$ , one finds analytically that  $Z(\kappa) \propto \kappa$ . In addition, for  $\kappa = \infty$ , both the time dependence  $M(\tau)$  and the prefactor  $Z(\kappa)$  can be calculated *exactly*. One finds, e.g., the remarkable result  $Z(\infty) = 2^{3/7} 3^{-9/7} e^{-\pi/7} \sqrt{3}$ .

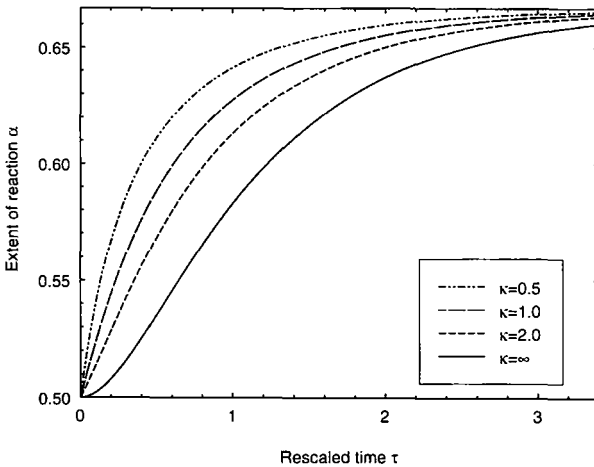


Fig. 2. The extent of reaction  $\alpha(t)$  as a function of the rescaled time variable  $\tau \equiv \kappa(t - t_c)/t_c$ , for  $f=3$  and various values of the sol-gel rate constant:  $\kappa = 0.5, 1.0, 2.0, \infty$ .

#### 4. SUMMARY AND DISCUSSION

In this paper I reviewed several kinetic models for aggregation beyond the gel point, notably those proposed by Flory, Stockmayer, and Ziff and Stell. In addition I proposed a new two-parameter class of models that retains the restriction that all clusters be acyclic and allows for different rate constants for sol–sol and sol–gel reactions. I showed that this *generalized acyclic model* (GAM) is exactly solvable in terms of standard (hypergeometric) functions and discussed the properties of the solution in various limits. A graphical representation of various physical quantities was generated numerically.

The solution presented here focuses on the  $RA_f$ -model, which describes the polymerization of monomers carrying  $f$  reactive A-groups. Accordingly,  $f \in \mathbb{N}$  in chemistry. It should be noted, however, that in our theory  $f$  is merely a parameter, which might equally well be taken real ( $f \in \mathbb{R}$ ), with  $f > 2$  in order to obtain gelation. Also note that the GAM can easily be formulated for other polymerization models, such as the so-called  $A_fRB_g$ -model (where monomers carry  $f$  A-groups and  $g$  B-groups and only A–B bonds are allowed).

A generalization of the GAM that includes also Flory's model is obtained if, in addition to sol–gel reactions with rate constant  $\kappa_1$ , one allows also for *cross-linking in the gel*, with rate constant  $\kappa_2$ . The size distribution of this  $(\kappa_1, \kappa_2)$ -model has again the form (6). One finds two coupled nonlinear first-order differential equations for  $\alpha_x$  and  $[A_x^F]$  as functions of  $M$ , which can be solved at least numerically. The time dependence of  $M(t)$  then follows from a third, separable equation for  $\dot{M}$ , similar to (9b).

Another extension would be the inclusion of *fragmentation*. The description of fragmentation of *finite size* clusters is by now well known.<sup>(11)</sup> In the *post-gel* stage, one has to allow also for fragmentation of the gel. Accordingly, a term of the form  $+\lambda b_k(\alpha)$  has to be added to (5), where  $\lambda$  is the fragmentation strength and  $b_k(\alpha)$  is the concentration of gel bonds joining a cluster of size  $k$  to the rest of the gel. Then Eq. (5) has to be supplemented with an appropriate kinetic equation for  $b_k(\alpha)$ . A possible exact solution of the GAM in the presence of fragmentation would clearly be of interest, since the explicit form of  $b_k(\alpha)$  might reveal many details of the gel structure, including its dependence on the sol–gel rate constant.

As a last possible extension I would like to mention the study of *spatial fluctuations*, which are neglected in the present rate equation approach. Spatial fluctuations have already been investigated in detail<sup>(12)</sup> for the special model  $K_{ij} = ij$ , which corresponds to the high-functionality limit of the third model ( $\kappa = 1$ ). It would certainly be of fundamental interest if the results of ref. 12 could be extended to the GAM at finite values of  $f$ .

## ACKNOWLEDGMENTS

Special thanks go to Matthieu Ernst for innumerable and invaluable discussions on physics, including aggregation. I also acknowledge helpful correspondence with Dr. R. M. Ziff (University of Michigan). This work is supported in part by the Deutsche Forschungsgemeinschaft under SFB 341.

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