

Reversible aggregation in self-associating polymer systems

Tomàs Sintes

Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain

Raúl Toral

Departament de Física, Universitat del les Illes Balears, E-07071 Palma de Mallorca, Spain

Amitabha Chakrabarti

Department of Physics, Kansas State University, Manhattan, Kansas 66506

(Received 25 January 1994)

We have studied the reversible aggregation process in self-associating polymer systems and carried out a numerical study of an off-lattice coalescence model in three dimensions. Extensive numerical simulations support a mean field description in terms of a generalized Smoluchowski equation and scaling relations.

PACS number(s): 82.20.Wt, 61.41.+e, 05.40.+j

I. INTRODUCTION

Aggregation in self-associating polymer systems [1] has been an area of increasing interest during the past several years due to the unusual rheological properties associated with the generated structures and the potential technological applications of these materials [2]. Self-associating polymers are flexible macromolecules that contain a number of functional groups distributed along the chain that favors aggregation. These groups interact via short-range forces which mediate the formation of structures such as block copolymers, gels [3], and microemulsions [4]. The functional groups could be ionic [5], so that the nature of the interactions is electrostatic, or they could be hydrophobic [6], in which case the interactions between them take place in a polar solvent. Of special interest is the case where the associating sites or “stickers” are located at both ends of a flexible polymer chain. This is the architecture of the associative thickener molecules [7,8]. In these systems, the molecules have a long hydrophilic chain, soluble in water, and contain a number of hydrophobic functional groups at each end. The presence of the functional groups make these molecules capable of producing networks and have been the subject of extensive research due to their potential use as viscosity modifiers.

General growth models, such as diffusion-limited aggregation [9,10] and Eden models [11], have been successfully extended to self-associating polymer systems [12,13]. Previous work focused on the morphology characterization and developed scaling relations between the size of the aggregates (given in terms of the radius of gyration) and the relevant parameters of the system such as the degree of polymerization N and the number of chains contained in a cluster. Both irreversible [12] and reversible aggregation [13] have been considered. In the latter case, the reversible binding between the functional

groups models the more realistic situation, in which the bonds have a characteristic lifetime, related to the thermal fluctuations. The dynamics of the cluster formation was considered in Ref. [14] in which an irreversible aggregation model for associative thickeners was introduced. The main result in this irreversible case is that, for different initial monodisperse systems with a fixed monomer concentration, the mean cluster size $S(N, t)$ behaves as $S(N, t) \sim N^{-\gamma} t^\delta$ and the cluster size distribution $n_s(N, t)$, defined as the number of clusters of size s per unit volume at time t , obeys a scaling form in the following way:

$$n_s(N, t) = N^{-1} S(N, t)^{-2} \phi(s/S(N, t)) , \quad (1)$$

where N is the chain length and $u = s/S(N, t)$.

A more general and realistic description of the aggregation process should include the possibility that the aggregates could break into small pieces. This is the well known reversible aggregation process, which has been the subject of extensive theoretical and computer work in cluster formation of single-particle systems [15–19]. Polymers, in contrast to single particles, do have an intrinsic geometry associated with each single-chain conformation. This additional degree of freedom enters the cluster size distribution functions through N , the degree of polymerization. Furthermore, the screening effect, due to the hydrophilic part of the chain, inhibits aggregation and may lead to a dramatically different cluster size distribution function. It is the purpose of this paper to study how the chain geometry, in the presence of a limited number of functional groups, affects the cluster formation of self-associating polymer systems in a reversible aggregation process.

The reversible aggregation process can be schematically represented by the following reaction mechanism:

$$A_i + A_j \xrightleftharpoons[F(N, i, j)]{K(N, i, j)} A_{i+j} ,$$

where A_i denotes a cluster containing i elementary units (an i -mer) and $K(N, i, j)$ and $F(N, i, j)$ are forward and reverse rate coefficients representing the coagulation and fragmentation processes, respectively. An elementary unit should be understood in our case as a polymer of chain length N . In a mean field description, the evolution of the cluster size distribution in this process, under the assumption of binary collisions, is given by the generalized Smoluchowski equation (to be referred as GS) [20]

$$\begin{aligned} \frac{dn_s}{dt} = & \frac{1}{2} \sum_{i+j=s} [K(N, i, j)n_i n_j - F(N, i, j)n_s] \\ & - \sum_{j=1}^{\infty} [K(N, s, j)n_s n_j - F(N, s, j)n_{s+j}] . \end{aligned} \quad (2)$$

This equation provides the time variation of the s -mer concentration $n_s(N, t)$ in terms of gains and losses due to different reactions in the sample. $K(N, i, j)$ is the coagulation kernel, giving the aggregation reaction rate of an i -mer with a j -mer. This kernel contains the i and j dependence of the meeting probability of an i -mer and a j -mer and includes effects such as the mass dependence of the collision cross section and the diffusion constant. $F(N, i, j)$ is the fragmentation kernel describing the breakup of an $(i + j)$ -mer into an i -mer and a j -mer.

The competition between coagulation and fragmentation processes may lead to a final steady-state configuration. There the mean cluster size $S(N, \kappa, t = \infty)$ is expected to be determined by the breakup constant κ , measuring the relative strength of the kernels for fragmentation and coagulation reactions and the chain length N . For small κ or for sufficiently large mean cluster size, we will assume that $S(N, \kappa, t = \infty)$ decreases according to the expression

$$S(N, \kappa, t = \infty) \sim N^{-\gamma} \kappa^{-\nu} , \quad (3)$$

which is a generalization of the behavior observed in the single-particle reversible aggregation [16]: $S(\kappa, t = \infty) \sim \kappa^{-\nu}$. We also assume that the dynamical scaling ansatz, known to be valid for pure aggregation processes [14], holds in a reversible process for all times up to the steady state regime, namely, $n_s(N, \kappa, t) \sim N^{-1} S(N, \kappa, t)^{-2} \phi(u)$, with $u = s/S(N, \kappa, t)$.

To determine the validity of the description of the evolution process in terms of scaling laws and mean field equations, we present in this paper the results of an extensive numerical study of a three-dimensional model for reversible aggregation of polymers. In this model, which is an off-lattice extension of the chain coalescence model introduced in Ref. [14], polymers are represented by a

succession of hard spheres (“pearl-necklace” model [21]). When two end spheres (stickers) belonging to different chains meet, the two chains coalesce and adopt the spatial configuration of one of them (chosen at random) with a mass equal to the sum of the masses of the initial chains. We have paid attention to both dynamical and steady-state scaling behaviors. We find that the mean cluster size and the size distribution at the steady state can be described in terms of scaling relations. The time evolution of the mean cluster size, starting from the aggregation dominated regime to the steady-state limit, is compatible with the predictions arising from the GS equation and the proposed scaling relations.

The rest of the paper is organized as follows. In Sec. II we deduce the Smoluchowski equation from the master equation obtained from probability considerations. In Sec. III we present a theoretical review of the reversible aggregation process for polymer systems. In Sec. IV we describe the numerical procedure. In Sec. V A we present a study of the irreversible aggregation process. In Sec. V B we compute the time evolution of the mean cluster size from the aggregation-dominated regime to equilibrium. Section V C deals with the steady-state limit for the cluster size distribution and the mean size. Section VI concludes with a discussion of the results.

II. DERIVATION OF THE SMOLUCHOWSKI EQUATION

In order to compare the dynamical evolution of the system toward the steady-state regime with the theoretical predictions coming from the GS equation, we find it interesting to develop the correspondence between the simulations and the GS equation. The objective is twofold: to outline the approximations necessary to obtain the GS equation from the microscopic rules governing the reversible aggregation process and to precisely establish the correct time unit needed for comparison. Our reasoning is rather general and independent of whether the constituent elements of the clusters are polymers or single-particle-like.

Let us define $N_s(t)$ as the mean number of clusters of size s at time t . The Smoluchowski equation is usually written in terms of the number density of clusters $n_s(t)$, defined as $N_s(t)/V$, where V is the (constant) volume of the system. We shall derive now the Smoluchowski equation from probabilistic considerations. For the sake of clarity we shall consider separately the fragmentation and aggregation process.

A. Pure fragmentation

Let us assume first that only fragmentation processes take place. Consider a cluster of size s , selected at random according to a probability $\hat{n}_s(\tau)$, and fragment it

into two pieces i, j such that $i + j = s$. We define $P(N_s(\tau) = M)$ to be the probability that at the simulation time τ the number of clusters of size s is exactly equal to M . We can write an evolution equation for this probability. Every time we select and try to fragment a cluster, time increases by a constant amount $\delta\tau$. With the above definitions we have the relation

$$\begin{aligned} P(N_s(\tau + \delta\tau) = M) &= P(N_s(\tau) = M)p_1 \\ &+ P(N_s(\tau) = M + 1)p_2 \\ &+ P(N_s(\tau) = M - 1)p_3 \\ &+ P(N_s(\tau) = M - 2)p_4, \end{aligned} \quad (4)$$

where

$$\begin{aligned} p_1 &= \text{prob[that } N_s(\tau) \text{ is not changed]}, \\ p_2 &= \text{prob(of selecting a cluster of size } s \text{ and fragment it)}, \\ p_3 &= \text{prob(of selecting a cluster of size } s' > s \text{ and fragment it in } s, s' - s \neq s), \\ p_4 &= \text{prob(of selecting a cluster of size } 2s \text{ and fragment it in } s, s). \end{aligned}$$

Let $F(i, j)$ be the conditional probability that, once selected, a cluster of size $i + j$ is fragmented into two clusters, the first one of size i and the second one of size j , considering the reverse order in i and j to be a different outcome. We can then write explicitly the probabilities appearing in the above expression as follows: $p_1 = [\text{probability of selecting any size } i < s \text{ and do whatever (fragment or not fragment)}] + (\text{probability of selecting a cluster of size } s \text{ and do not fragment it}) + (\text{probability of selecting a cluster of size } i > s \text{ and do not fragment it into pieces of sizes } i, i - s)$. This in equation form reads

$$\begin{aligned} p_1 &= \sum_{i=1}^{s-1} \hat{n}_i(\tau) + \hat{n}_s(\tau) \left(1 - \sum_{i=1}^{s-1} F(i, s - i) \right) \\ &+ \sum_{i>s} \hat{n}_i(\tau) [1 - 2F(s, i - s)] + \hat{n}_{2s}(\tau) F(s, s), \end{aligned} \quad (5)$$

where $\hat{n}_s(\tau)$ is the probability of selecting a cluster of size s at time τ . Reasoning in this way, the other probabilities appearing in Eq. (4) are given by

$$p_2 = \hat{n}_s(\tau) \sum_{i=1}^{s-1} F(i, s - i), \quad (6)$$

$$p_3 = 2 \sum_{i>s} \hat{n}_i(\tau) F(s, i - s) - 2\hat{n}_{2s}(\tau) F(s, s), \quad (7)$$

$$p_4 = \hat{n}_{2s}(\tau) F(s, s). \quad (8)$$

Introducing these expressions in Eq. (4) and applying the relation

$$N_s(\tau) = \sum_M M P(N_s(\tau) = M), \quad (9)$$

we arrive, after some algebra, at

$$\begin{aligned} N_s(\tau + \delta\tau) - N_s(\tau) &= -\hat{n}_s(\tau) \sum_{i=1}^{s-1} F(i, s - i) \\ &+ 2 \sum_{i>s} \hat{n}_i(\tau) F(s, i - s). \end{aligned} \quad (10)$$

The standard procedure used in numerical simulations is such that a cluster is selected at random with a probability independent of its size. We can then, in the

mean field spirit of the Smoluchowski equation, take $\hat{n}_i(\tau) = N_i(\tau)/N(\tau)$, where $N(\tau) = \sum_j N_j(\tau)$ is the total number of clusters at time τ . By using this relation, it follows that

$$\begin{aligned} \frac{N_s(\tau + \delta\tau) - N_s(\tau)}{N(\tau)^{-1}} &= -N_s(\tau) \sum_{i=1}^{s-1} F(i, s - i) \\ &+ 2 \sum_{i>s} N_i(\tau) F(s, i - s). \end{aligned} \quad (11)$$

If we introduce the unit of rescaled time δt as

$$\delta t = \frac{\delta\tau}{N(\tau)}, \quad (12)$$

we have (substituting the difference by a derivative and setting $\delta\tau = 1$, which stands for a trial in the simulation)

$$\frac{\partial N_s(t)}{\partial t} = -N_s(t) \sum_{i=1}^{s-1} F(i, s - i) + 2 \sum_{i>s} N_i(t) F(s, i - s). \quad (13)$$

Dividing by the system volume V one obtains exactly the fragmentation part of the GS equation for the cluster size distribution density except for a factor of 2 because in the definition given above $F(i, j)$ and $F(j, i)$ are considered to be different events. This double counting has to be taken into proper account in the definition of the fragmentation probability in the numerical model.

The relevant point we may notice here is that the elementary time δt is related to the simulation time in a natural way. Every time we choose a cluster and try to break it, *time should be incremented by a quantity equal to the inverse of the total number of clusters present at that time*. We shall call this time a *Monte Carlo time step*.

B. Pure aggregation

It is possible to get the aggregation part of the Smoluchowski equation using a method similar to the one above and considering some mean-field-like hypothesis. If one notes that the probability that two clusters of sizes i and j aggregate to form a cluster of size $i + j$ is proportional to the probability of selecting these two clusters times the

probability that the proposed aggregation is accepted, then the resulting equation is

$$N_s(\tau + \delta\tau) - N_s(\tau) = \sum_{i+j=s} K(i, j) \hat{n}_i(\tau) \hat{n}_j(\tau) - 2 \sum_{j=1}^{\infty} K(s, j) \hat{n}_s(\tau) \hat{n}_j(\tau) \quad (14)$$

(again, double counting is present in the reaction kernels). Now we have to decide whether a numerical simulation satisfies the hypothesis that leads to this equation. Let us consider only the term $K(i, j) \hat{n}_i(\tau) \hat{n}_j(\tau)$, which represents the probability that clusters of sizes i and j aggregate. Suppose that in the simulation, a cluster of size i is selected first and then it is moved randomly to another location, *uncorrelated to the previous position*. Then the probability of finding a cluster of size j is $N_j(\tau)v/V$, v being the effective volume of a single cluster and V the total volume of the system. Finally these two clusters do aggregate with probability $k(i, j)$. In this case we have then

$$K(i, j) \hat{n}_i(\tau) \hat{n}_j(\tau) = \hat{n}_i(\tau) N_j(\tau) \frac{v}{V} k(i, j) = N_i(\tau) N_j(\tau) \frac{v}{V} k(i, j) \frac{1}{N(\tau)}. \quad (15)$$

Substituting this in Eq. (14), multiplying by $N(\tau)$, using the same definition of time t , and dividing by V , one gets the aggregation part of the Smoluchowski equation

$$\frac{\partial n_s(t)}{\partial t} = \sum_{i+j=s} k(i, j) v n_i(t) n_j(t) - 2 \sum_{j=1}^{\infty} k(s, j) v n_s(t) n_j(t). \quad (16)$$

Again this is the usual way of writing the Smoluchowski equation, but now the aggregation kernel is identified as a geometric factor, giving the volume occupied by a cluster times the probability that these two clusters do aggregate when brought into contact. Note again that the natural time that appears here is the time which is increased by an amount inverse to the number of present clusters.

III. THEORETICAL REVIEW

We briefly review the main predictions of the GS equation for the mean cluster size evolution. We incorporate the polymer effect by assuming that the chain structure is reflected via a power-law dependence on the chain length for the reaction kernels, so that the coagulation and fragmentation kernels are represented by

$$K(N, i, j) = vk(N, i, j) = v\kappa_c N^{-\theta} \psi(i, j) \quad (17)$$

and

$$F(N, i, j) = \kappa_f N^\omega \Phi(i, j), \quad (18)$$

with $\psi(1, 1) = \Phi(1, 1) = 1$ and κ_c and κ_f being the coagulation and breakup constants, respectively. We assume a scaling behavior for the cluster size distribution as

$$n_s(N, \kappa, t) = M_1 S(N, \kappa, t)^{-2} \varphi(u), \quad (19)$$

with $u = s/S(N, \kappa, t)$. M_1 is the first moment in the size distribution and represents the total density of chains in the system. As we are interested in the N dependence of the mean size evolution and the time to reach equilibrium, we consider systems with constant density ρ_T , such that the total number of monomers is preserved. Therefore, $M_1 = \rho_T N^{-1}$. The moments are calculated in the usual way

$$M_i = \sum_{s=1}^{\infty} s^i n_s(N, \kappa, t) \quad (20)$$

and the mean cluster size is defined as

$$S(N, \kappa, t) = M_1/M_0. \quad (21)$$

As commonly assumed in literature [16–19], the kernels are taken to be homogeneous functions of their arguments, so that $\psi(ai, aj) = a^\lambda \psi(i, j)$ and $\Phi(ai, aj) = a^\alpha \Phi(i, j)$. After writing the equation for the time derivative of the zeroth moment, one finally finds a differential equation for $S(N, \kappa, t)$:

$$\frac{d}{dt} S(N, \kappa, t) = I_1 M_1 v \kappa_c N^{-\theta} S^\lambda - I_2 \kappa_f N^\omega S^{\alpha+2}, \quad (22)$$

where

$$I_1 = \int_0^\infty dx \int_0^\infty dy \psi(x, y) \varphi(x) \varphi(y), \quad (23)$$

$$I_2 = \int_0^\infty dx \int_0^\infty dy \Phi(x, y) \varphi(x+y). \quad (24)$$

Rewriting Eq. (22) in terms of the reduced variables

$$\hat{s} = \frac{S(N, \kappa, t)}{S(N, \kappa, \infty)} \quad (25)$$

and

$$\hat{t} = \frac{t}{\zeta}, \quad (26)$$

one obtains the scaled equation

$$\frac{d}{d\hat{t}} \hat{s} = \hat{s}^\lambda - \hat{s}^{\alpha+2}. \quad (27)$$

Then the mean cluster size at steady state is found to be

$$S(N, \kappa, \infty) = \left(\frac{I_1 \rho_T v \kappa_c N^{-(\theta+\omega+1)}}{I_2 \kappa_f} \right)^y \quad (28)$$

and the characteristic time to approach equilibrium is

$$\zeta = \frac{S(N, \kappa, \infty)^{1-\lambda}}{I_1 \rho_T v \kappa_c N^{-(\theta+1)}}, \quad (29)$$

where

$$y = (\alpha - \lambda + 2)^{-1}. \quad (30)$$

Also, from Eq. (3) we get a relation for the exponent γ as

$$\gamma = y(\theta + 1 + \omega). \quad (31)$$

IV. NUMERICAL MODEL

To test the scaling predictions for the cluster size distribution and the time evolution of the mean cluster size, we have carried out extensive numerical simulations in three-dimensional off-lattice systems. We have considered a *pearl-necklace model* [21] for the polymer chains, enclosed in a cubic cell of dimensions $L \times L \times L$, where L is equal to 50 times the monomer diameter. Our simulation starts with a monodisperse initial configuration. This has been obtained by randomly placing a number of chains of length N in the cell in such a way that the monomers cover 15% of the total volume available. The initial configuration is equilibrated by random movements without aggregation. The excluded-volume criterion is assumed, so that none of the monomers is allowed to overlap with each other.

We choose, at random, one of the clusters, initially identified with chains, and try to move it by executing a reptation-type motion in a forward or reverse direction, also chosen at random. The excluded-volume criterion is also applied here, except for the sticker sites, which may overlap with another sticker belonging to a different chain. If this overlap between stickers takes place, then the corresponding chains aggregate and form a cluster.

In order to avoid the complexity arising from the geometrical structure of the clusters, which should be reflected in the functional form of the reaction kernels, we employ the so-called *chain coalescence model* [14]. In this model, the clusters are defined to be single chains with the same length as the initial ones. When two clusters of masses i and j interact, they coalesce into a heavier cluster which has the shape of either the i th or the j th chain, but a mass of $i + j$. The rate of this interaction is proportional to the reaction kernel $K(N, i, j)$. Since the clusters have the same chain geometry, the functional form of the reaction kernel can be specified exactly. In our simulation we have assumed a mass-independent sticking probability, so that the aggregation kernel is constant and $\psi(i, j)$ is set to 1. This gives $\lambda = 0$. Furthermore we consider $\kappa_c = 1$ (and then κ should be identified with κ_f), which yields simply, for the aggregation kernel,

$$K(N, i, j) = vN^{-\theta}. \quad (32)$$

The probability of choosing a cluster of mass $s = i + j$ is given by $\hat{n}_s(N, \kappa, t)$, and we consider that any of the $s - 1$ bonds can be broken with equal probability. Then, the probability of breaking one of the $s - 1$ bonds of a cluster of size s can be written as

$$\hat{n}_s(N, \kappa, t) \frac{1}{s-1} p(s), \quad (33)$$

where $p(s)$ is considered to have the functional form

$$p(s) = \kappa_f (s-1) s^\alpha, \quad (34)$$

so that

$$F(N, i, j) = \kappa_f N^\omega \Phi(i, j) = \kappa_f (i + j)^\alpha \quad (35)$$

and $\omega = 0$. Note that double counting in our probability definition is present, in agreement with the deduction of the pure fragmentation equation (13). Therefore Eqs. (30) and (31) become

$$y = (\alpha + 2)^{-1} \quad (36)$$

and

$$\gamma = y(\theta + 1) \quad (37)$$

and the constants α and κ are the only parameters in the model. In the simulation, a cluster is picked at random and an attempt is made either to break it or to move it in a random fashion. If we attempt to break a cluster of size $s = i + j$, it will break with a probability given by $p(s)$. The new position of one of the two fragments will remain the same as the original cluster and the other one, represented by a new chain of length N , is placed at a random location inside the cell, preserving the excluded-volume criteria. This situation corresponds to the so-called *uncorrelated fission*: the resulting fragments are placed at random, uncorrelated positions, in the spirit of the mean field theory [18]. This choice of uncorrelated fission, with the fact that the resulting geometry of clusters is neglected, makes it plausible that the process is described by the GS equation with single choices for the fragmentation and aggregation kernels.

In a general computer simulation, where long-range forces are present, each cluster C_i can potentially interact with any of the remaining aggregates. However, for short-range interactions, a significant amount of computer time, used in determining which pairs of clusters are close enough to interact, can be reduced. In order to achieve this, one should be able to efficiently compute the subset of clusters with which C_i interacts. For this reason we have implemented a *link cell* method [22]. In this scheme the simulation cell is broken into N_c smaller subcells. Then to each subcell we assign a list of clusters belonging to it. If the edge length of each cell L_c is chosen to be larger than the diameter of the particles, then all interacting pairs are located within the same cell or in one of the 26 adjoining cells. Therefore, the time to find all interacting pairs of clusters scales with the actual number of clusters, say C_t , instead of C_t^2 for the standard method. For each pair of values (κ, α) , the maximum number of subcells N_c is chosen in order to minimize the CPU time.

V. RESULTS AND DISCUSSION

A. Irreversible fragmentation process

Before studying the more general reversible aggregation case, we have focused on the irreversible fragmenta-

tion process. Our purpose is to check, first, the equivalence between the Monte Carlo time step and the elementary time unit in the GS equation and, second, the validity of the fragmentation kernel under the assumption of an effective probability to break a cluster given by $p(s)$ [Eq. (34)].

For the present purpose we write the fragmentation kernel $F(N, i, j)$ as

$$F(N, i, j) = \kappa_f (i + j)^\alpha. \quad (38)$$

For this particular choice of $F(N, i, j)$, the equation for the pure fragmentation process reads

$$\frac{dn_x}{dt} = \kappa_F \left[-x^\alpha (x-1)n_x + 2 \sum_{i=1}^{\infty} (x+i)^\alpha n_{x+i} \right]. \quad (39)$$

This equation can be solved approximately [23] and for a monodisperse initial condition $n_x(t=0) = \delta(x-l)$ the solution is

$$n_x(t) = \begin{cases} 2\kappa_F t l^\alpha e^{-\kappa_F t x^{\alpha+1}}, & x < l \\ \delta(x-l) e^{-\kappa_F t x^{\alpha+1}}, & x = l \\ 0, & x > l. \end{cases} \quad (40)$$

In order to test the range of validity of the above solution, we have integrated numerically the set of equations (39) by using a fourth-order Runge-Kutta method with a variable time step. This set was truncated to a finite number of equations by setting the initial condition to a single cluster of mass equal to l . We have computed the mean cluster size $S(t)$, defined in Eq. (21), both from the approximate solution and by numerically integrating Eq. (39). We have also carried out numerical simulations for the irreversible aggregation process by itself. We set the initial configuration to be a single cluster of mass l . In this model we pick a cluster at random (if there is more than one cluster) and attempt to break it with a probability given by $p(s)$, where s is the cluster size. Care must be taken as how l , κ_F , and α are chosen since $p(s)$, interpreted as a probability, must satisfy $p(l) \leq 1$. The results show excellent agreement between the numerically integrated system, the approximate analytical solution, and the simulation data, as can be seen in Fig. 1. In this figure we have plotted, in a logarithmic scale, the mean cluster size $S(t)$ as a function of time for these particular values: $l = 1000$, $\alpha = 1$, and $\kappa_F = 10^{-6}$. Furthermore, in the case of $l \rightarrow \infty$, the mean cluster size coming from the approximate solution is found to scale as

$$S(t) \sim (\kappa_f t)^{-\frac{1}{\alpha+1}}. \quad (41)$$

This behavior is also shown in Fig. 1, where we get a slope of -0.5 , which corresponds to the exponent $-\frac{1}{\alpha+1}$ for $\alpha = 1$.

B. Dynamical evolution

In order to test the validity of Eq. (27), we have solved it for different values of α ranging from $\alpha = -0.5$ to $\alpha = 2$. The initial condition for the mean cluster

size is $\hat{s}(t=0) = 1/S(N, \kappa, \infty)$, corresponding to the monodisperse distribution considered before. We have also performed numerical simulations for the same values of α and computed the mean cluster size $S(N, \kappa, t)$ from $t = 0$ up to the steady-state regime. The results have been averaged over ten different initial configurations. We have also varied the breakup constant from $\kappa = 10^{-5}$ to $\kappa = 10^{-3}$ and considered chain lengths of $N = 5, 10, 20, 30$, and 40 .

To rescale the simulation data we must determine I_1 and the exponent θ . Since $K(N, i, j) = \nu N^{-\theta}$ and $\psi(i, j) = 1$ in our system, Eq. (23) reads

$$I_1 = \left[\int_0^\infty dx \varphi(x) \right]^2. \quad (42)$$

It is straightforward to see that $I_1 = 1$. The exponent θ can be obtained by considering the pure aggregation process. It is well known that the Smoluchowski equation for the irreversible aggregation process, that is, for $F(N, i, j) = 0$, and for a constant reaction kernel $K(N)$ can be solved explicitly. The exact solution predicts [9]

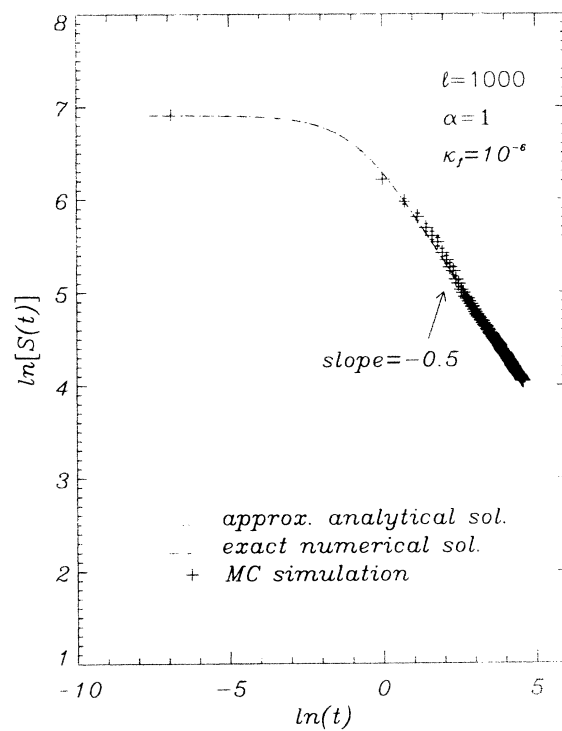


FIG. 1. Logarithmic plot of $S(t)$ vs t corresponding to an irreversible fragmentation process for an initial monodisperse distribution $n_x(t=0) = \delta(x-l)$. The dashed line comes from the numerical integration of Eq. (39). The dotted line is the approximated solution of $S(t)$ calculated from Eq. (40). We also plot (+) the result of a Monte Carlo simulation of an irreversible fragmentation process with a breakup probability given by $p(s) = \kappa(s-1) s^\alpha$, where s is the size of the cluster trying to be broken. We have considered the particular case of $l = 1000$, $\alpha = 1$, and $\kappa_f = 10^{-6}$. Observe that for $t \geq 1$ the slope of the curve corresponds to the value $-\frac{1}{\alpha+1}$ supporting the scaling relation (41).

$$S(N, t) = S(N, t = 0) + M_1 K(N) t. \quad (43)$$

Substituting $K(N)$ by its actual expression, the relation (43) can be written as

$$S(N, t) = S(N, t = 0) + \rho_T v N^{-(\theta+1)} t. \quad (44)$$

We have simulated the irreversible aggregation process for different values of the chain length N . In Fig. 2 we represent $S(N, t)$ as a function of t . According to the expression (44), the slopes of the curves are given by $\xi(N) = \rho_T v N^{-(\theta+1)}$ (note that they are independent of α and κ). We can rewrite Eq. (29) to obtain the characteristic time ζ to reach the steady state, in terms of $\xi(N)$:

$$\zeta = \xi(N)^{-1} S(N, \kappa, \infty). \quad (45)$$

Once $\xi(N)$ and $S(N, \kappa, \infty)$ have been directly determined from the simulation data, we can compare the theoretical evolution of the mean cluster size with the simulation data. We have plotted in Fig. 3 the result for different choices of N , κ , and α . Observe the excellent agreement between simulation and the integration of Eq. (27) without any further parameter fitting. As expected, after a sufficient long time, the mean cluster size becomes time independent and reaches its saturation value $S(N, \kappa, \infty)$.

By fitting $\xi(N) = \rho_T v N^{-(\theta+1)}$, we can determine the value $\theta = 0.1 \pm 0.02$. Moreover, from Eq. (44) we know

that the mean cluster size scales as $S(N, t) \sim N^{-(\theta+1)} t$. To be able to compare results for different values of N , we need to set the same time scale for all systems. This is simply done taking $\tilde{t} = t/N$ as the time unit, since we consider systems with constant density ρ_T . In Fig. 4 we have plotted $S(N, \tilde{t}) N^\theta$ vs \tilde{t} in a logarithmic scale. It seems clear that the data collapse on a single master curve. The estimated value of the exponent θ is $\theta = 0.1 \pm 0.01$.

C. Steady-state limit

Because of the fragmentation process, the system reaches a steady-state regime after a sufficiently long time. Afterward, the mean number of clusters and hence the mean cluster size remain constant. In this regime the theory predicts that the exponents y and γ obey the algebraic relations (36) and (37), respectively. Once we have determined the value of θ , we turn back to the reversible aggregation mechanism. Our purpose is to determine the value of the exponents y and γ and to test the scaling relation Eq. (28). To this end we have computed, for different sets of N , κ , and α , the mean size $S(N, \kappa, \infty)$ and cluster size distribution $n_s(N, \kappa, \infty)$, once the system reaches the steady state. We have averaged these quantities over 1000 measurements.

To compute the exponent y we have plotted the mean cluster size $S(N, \kappa, \infty)$ versus the breakup constant κ in

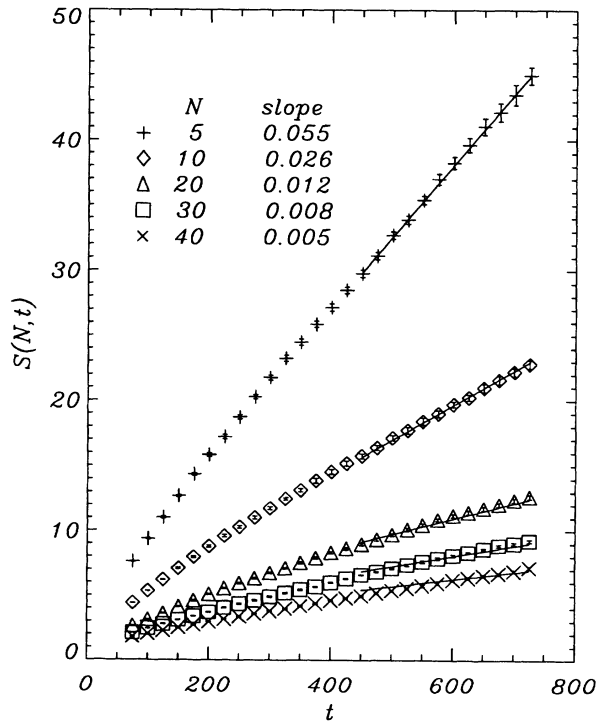


FIG. 2. Plot of the mean cluster size $S(N, t)$ as a function of time t . The solid lines correspond to the slopes of the curves also indicated in the figure. These values are the ones assigned to $\xi(N)$ used in determining the characteristic time ζ [Eq. (45)].

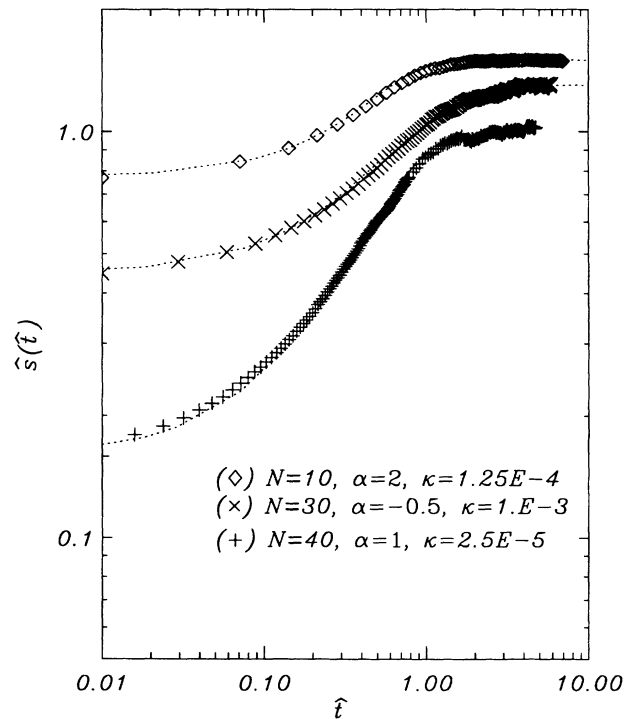


FIG. 3. Log-log plots of the reduced variable \hat{s} vs \hat{t} for different values of N , α , and κ . Each plot has been shifted an arbitrary amount in the vertical axis for the sake of clarity. Observe the good agreement between simulation data and the curves coming from the solution of Eq. (27) (dotted lines).

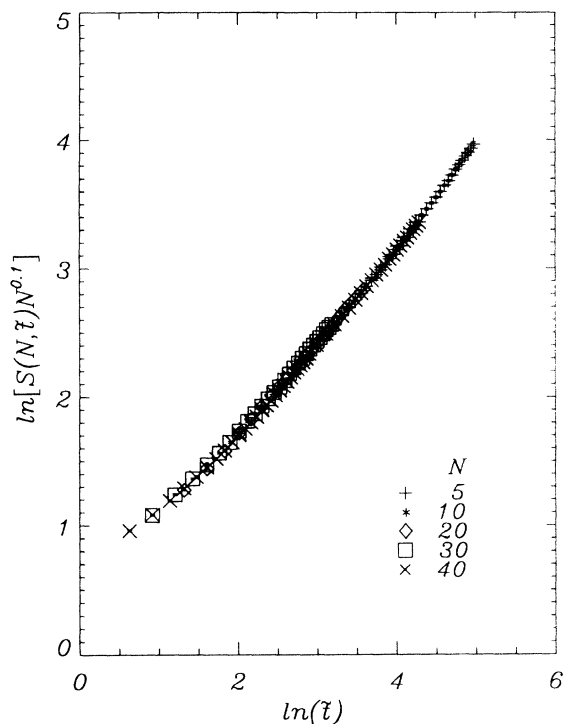


FIG. 4. Logarithmic plot of $S(N, \bar{t})N^\theta$ vs $\bar{t} = t/N$ for different values of N . This plot corresponds to the simulation of the irreversible aggregation process. We obtained $\theta = 0.1 \pm 0.01$. Note that all data collapse reasonably well in a single master curve, supporting Eq. (44)

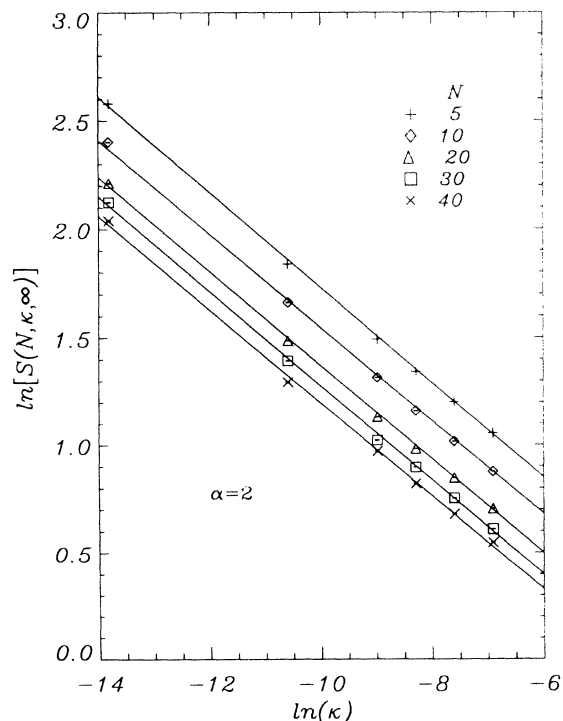


FIG. 5. Logarithmic plot of the mean cluster size $S(N, \kappa, \infty)$ vs the breakup constant κ for $\alpha = 2$. We have considered the chain length to be $N = 5, 10, 20, 30$, and 40 . The slope of the curves gives the value of the exponent y . The best least-squares fit to the data gives $y = 0.22 \pm 0.01$. The expected theoretical value is $y = 0.25$.

TABLE I. y and γ values obtained with our numerical model compared with the theoretical mean-field expected ones for different α 's. The asterisk denotes setting $\theta = 0.1 \pm 0.02$.

α	y_{th}	y	γ_{th}^*	γ
-0.5	0.67	0.62 ± 0.03	0.733 ± 0.013	0.65 ± 0.05
0.5	0.40	0.35 ± 0.02	0.440 ± 0.008	0.40 ± 0.02
1.0	0.33	0.29 ± 0.02	0.367 ± 0.006	0.33 ± 0.02
2.0	0.25	0.22 ± 0.01	0.275 ± 0.005	0.25 ± 0.02

a logarithmic scale. We have considered the chain length N to take the values $N = 5, 10, 20, 30$, and 40 . In Table I we list the values obtained from the best least-square fit to the data compared with the theoretical predicted ones from Eq. (36). We observe reasonable agreement between them, although the simulation obtained values tend to be smaller than the predicted ones. In Fig. 5 we show a plot corresponding to the case for $\alpha = 2$.

To estimate the value of the exponent γ , we have computed the slope of $S(N, \kappa, \infty)$ vs N curve, plotted in a logarithmic scale. For each α value we have considered seven different values of κ ranging from 10^{-6} to 10^{-3} . In Table I we tabulate the corresponding results. To obtain the theoretically expected γ value we have set $\theta = 0.1 \pm 0.02$. Observe the good agreement between the theoretical prediction and the numerical results for γ , within the error bars. In Fig. 6 we represent one

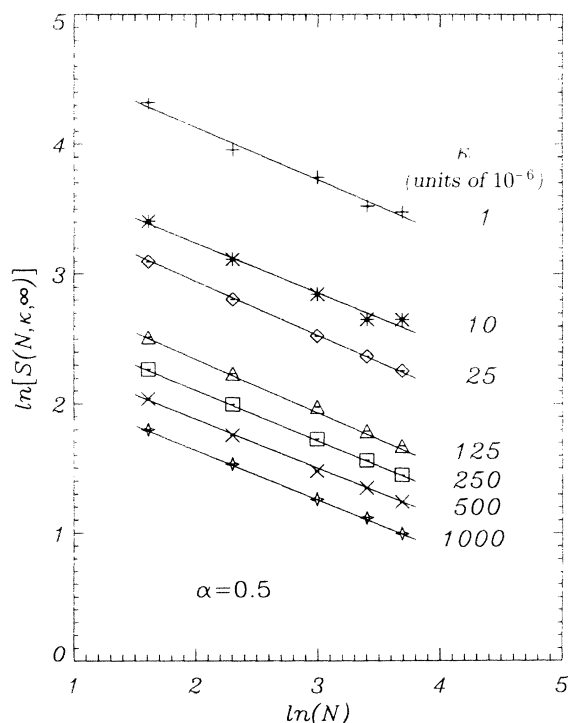


FIG. 6. Logarithmic plot of the mean cluster size $S(N, \kappa, \infty)$ vs the chain length N for $\alpha = 0.5$. We have considered seven different values of the breakup constant κ ranging from 10^{-6} to 10^{-3} . The slopes of the curves give $\gamma = 0.40 \pm 0.02$. The theoretically expected value for this particular α is $\gamma = 0.44$.

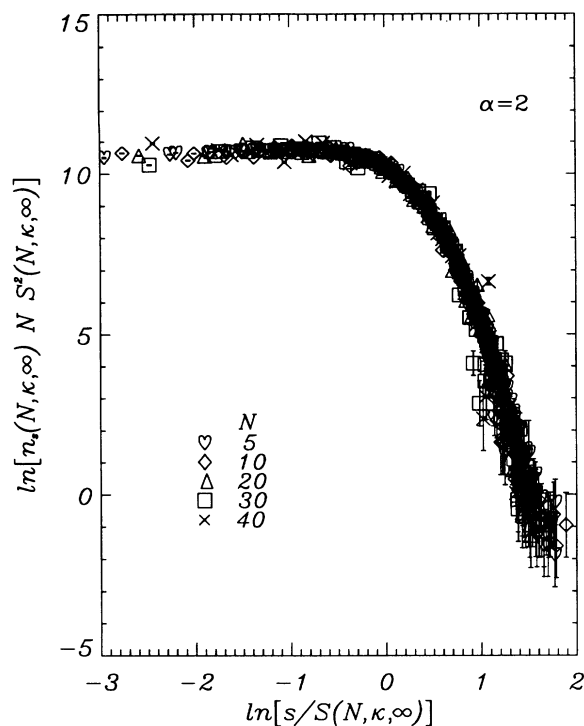


FIG. 7. Plot in a logarithmic scale of $n_s(N, \kappa, \infty) N S^2(N, \kappa, \infty)$ vs $s/S(N, \kappa, \infty)$ for different values of κ and N . $\alpha = 2$. Note that all data collapse reasonably well in a single master curve, supporting the scaling relation for the cluster size distribution at the steady-state region [Eq. (19)].

particular case corresponding to $\alpha = 0.5$.

To test the relationship (19) at the steady state ($t \rightarrow \infty$) we have plotted on a logarithmic scale $n_s(N, \kappa, \infty) N S^2(N, \kappa, \infty)$ vs $s/S(N, \kappa, \infty)$. Figure 7 show these results for $\alpha = 2$ and for all pairs (N, κ) . For simplicity, we have used different symbols just for different chain lengths N . We observe that all the data collapse reasonably well onto a single master curve, thus supporting the predicted scaling relation.

VI. CONCLUSIONS

In this paper we have studied the reversible aggregation process in associative thickener systems. We have developed a numerical model based on an off-lattice coalescence model in three dimensions. We have shown, by an explicit derivation of the generalized Smoluchowski equation, that the natural time that appears in the equation is the time which is increased by an amount inversely proportional to the number of clusters present in the numerical simulation at that particular instant.

We have carried out simulations for the pure irreversible fragmentation process, where we have found a scaling relation for the mean cluster size. For the reversible aggregation process we have paid attention to both dynamical and steady-state scaling behaviors. In the former case, we have studied the mean cluster size evolution from the aggregation dominated regime to the steady-state regime. We have found excellent agreement between theoretical predictions and numerical simulations, supporting the mean field description. We have computed the exponents γ and γ from the data for the mean cluster size at equilibrium. The results obtained are in good agreement, within the errors, with the theoretically predicted ones derived from proposed scaling relations and mean field theory. Small deviations observed might be explained in terms of the restriction imposed on the aggregation reaction kernel, on the basis of the assumption that the new position occupied by the cluster is uncorrelated to the previous location. This fact makes the theoretical model less realistic but, on the other hand, allows one to specify the value of the reaction kernel explicitly. Finally, we have verified the scaling ansatz for the size distribution at the steady-state regime.

ACKNOWLEDGMENT

Financial support from the DGICYT (Spain), Grant No. PB-92-0046, is acknowledged.

- [1] J. N. Israelachvili, *Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems* (Academic Press, New York, 1985).
- [2] E. J. Goethals, *Telechelic Polymers: Synthesis and Applications* (CRC Press, Boca Raton, FL, 1989).
- [3] D. S. Stauffer, A. Coniglio, and M. Adam, *Adv. Polym. Sci.* **44**, 103 (1982).
- [4] H. F. Eicke, *Micelles*, edited by M. J. S. Dewar (Springer, Berlin, 1980).
- [5] L. Holliday, *Ionic Polymers* (Halstead Press, New York, 1975).
- [6] K. Mittal, *Surfactants in Solution* (Plenum Press, New York, 1984).
- [7] *Water-Soluble Polymers: Beauty with Performance*, edited by J. E. Glass (American Chemical Society, Washington, D.C., 1986).
- [8] R. D. Jenkins, C. A. Silebi, and M. S. El-Aasser, *Proc. ACS Div. Polym. Mater. Sci. Eng.* **61**, 629 (1989); R. D. Jenkins, Ph.D. thesis, Lehigh University, 1990.
- [9] R. Ziff, in *Kinetics of Aggregation and Gelation*, edited by F. Family and D. Landau (North-Holland, Amsterdam, 1984).
- [10] R. Jullien and R. Botet, *Aggregation and Fractal Aggregates* (World Scientific, Singapore, 1987); T. A. Witten and L.M. Sander, *Phys. Rev. Lett.* **47**, 1400 (1981).
- [11] M. Eden, in *Proceedings of the Fourth Berkeley Symposium on Mathematical Statistics and Probabilities*, edited by E. Neymann (University of California Press, Berkeley, 1961), Vol. IV.
- [12] A. C. Balazs, C. Anderson, and M. Muthukumar, *Macromolecules* **20**, 1999 (1987); A. C. Balazs, F. E. Karasz, and W. J. Macknight, *Cell Biophys.* **11**, 91 (1987); A. Chakrabarti and R. Toral, *J. Chem Phys.* **91**, 5687 (1989); T. Sintes, R. Toral, and A. Chakrabarti, *ibid.*

- 94**, 5115 (1991).
- [13] A. C. Balazs, J. Hu, and A. P. Lentvorsi, *Phys. Rev. A* **41**, 2109 (1990).
- [14] A. Chakrabarti, D. Hong, and R. Toral, *J. Phys. A* **23**, L311 (1990).
- [15] P. G. van Dongen and M. Ernst, *J. Stat. Phys.* **37**, 301 (1984); M. Kolb, *J. Phys. A* **19**, L263 (1986).
- [16] F. Family, P. Meakin, and J. Deutch, *Phys. Rev. Lett.* **57**, 727 (1986).
- [17] C. Sorensen, H. Zhang, and T. Taylor, *Phys. Rev. Lett.* **59**, 363 (1987).
- [18] P. Meakin and M. Ernst, *Phys. Rev. Lett.* **60**, 2503 (1988).
- [19] R. Vigil and R. Ziff, *Phys. Rev. Lett.* **61**, 1431 (1988); *J. Colloid Interface Sci.* **133**, 257 (1989); I. Elminyaw, S. Gangopadhyay, and C. Sorensen, *ibid.* **144**, 315 (1991); T. Sintes, R. Toral, and A. Chakrabarti, *Phys. Rev. A* **46**, 2039 (1992).
- [20] M. von Smoluchowski, *Z. Phys. Chem.* **92**, 129 (1917); P. Blatz and A. Tobolski, *J. Phys. Chem.* **49**, 77 (1945); R. Cohen and G. Benedek, *ibid.* **86**, 3696 (1982).
- [21] A. Baumgärtner, in *Applications of the Monte Carlo Method in Statistical Physics*, 2nd ed., Topics in Current Physics Vol. 36, edited by K. Binder (Springer-Verlag, Berlin, 1987), Chap. 5.
- [22] M. Allen and D. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987); G. Grest, B. Dünweg, and K. Kremer, *Comput. Phys. Commun.* **55**, 269 (1989); R. Hockney and J. Eastwood, *Computer Simulations Using Particles* (McGraw-Hill, New York, 1981).
- [23] R. Ziff and E. McGrady, *J. Phys. A* **18**, 3027 (1985).