

LETTER TO THE EDITOR

Dynamical scaling in self-associating polymer aggregates

Amitabha Chakrabarti†, Daniel C Hong and Raul Toral‡

Department of Physics and Center for Polymer Sciences and Engineering, Lehigh University, Bethlehem, PA 18015, USA

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Abstract. We present a simple model that simulates the dynamics of the long flexible self-associating polymer chains immersed in water and develop a dynamical scaling description for the cluster size distribution function for irreversible aggregation. Each chain may have one or several functional groups at each end that can associate with one another. We find that the chain length is a new scaling variable that appears explicitly in the scaling function. The validity of our scaling predictions is confirmed by extensive computer simulations.

Self-associating polymers are flexible macromolecules containing a number of functional groups ('sticker sites') that effectively attract each other. These functional groups could be ionic [1], so that the interactions between them are electrostatic, or they could be hydrophobic [2], in which case the interactions between these sites are mediated by the aqueous medium. The effective strong interactions between these sites lead the chains to self-associate and form clusters [3]. Due to this mechanism, the rheological properties of these polymers in solution are dramatically changed, when compared to the 'pure' case where the functional groups are absent. Associative thickeners are one such class of self-associating polymers. In these systems, the molecules have a long hydrophilic chain, readily soluble in water, and contain a number of hydrophobic functional groups at each end of the long chains. Due to the presence of functional groups at each end of the chain, these molecules are capable of producing networks by self-association§, in contrast to the micelle formation [5] seen in polymers with one functional group end.

Recently, the associative thickeners are the subject of extensive research, primarily due to their potential use as viscosity modifiers in latex paint systems. Theoretical studies for the cluster formation in self-associative polymers have been carried out for the case of a single functional group end within a mean-field approach [6]. Also, association behaviour in the presence of shear flow is available in the literature [7] for the chains containing a number of functional groups along the chains. However, the dynamics of the cluster formation in these systems has not been considered in the above studies. On the other hand, the dynamics of cluster formation in single-particle aggregation is the subject of extensive theoretical [8-10], and experimental [8, 11] studies in recent years. In the theoretical investigation, one of the major objectives is

† Present address: Department of Physics, Kansas State University, Manhattan, KS 66506, USA.

‡ Permanent address: Departament de Física, Universitat de les Illes Balears, Palma de Mallorca, E-07071, Spain.

§ The idea of network formation is supported by the experimental observation that the sample with self-associating chains is transparent; see [4].

to study the dynamical scaling behaviour for the number of clusters for irreversible aggregation [8–10]. In contrast to the cluster formation of single particles, which are point-like, the self-associative chains, however, do have an intrinsic geometry associated with each single-chain conformation. This additional degree of freedom is expected to lead to a rather dramatic deviation from the usual cluster size distribution function observed in single-particle aggregation [8–11]. In view of this, we find it particularly interesting to study how the geometry of the flexible chains affects the cluster formation of the self-associative polymer chains with several functional groups. Recently, Debierre and Turban [12, 13] have simulated the chain–chain aggregation process in two [12] and in three [13] dimensions. They start with monomers placed in a lattice and study the coagulation between these monomers to form long chains—a model relevant to the polymerisation process, but not to the network formation in associative thickeners for example, where one considers long chains to start with. Also, in their model the chains move rigidly as in the case of cluster–cluster aggregation and the flexibility of the long chains are not taken into account. Thus, further studies are necessary to investigate the aggregation process in self-associative polymers.

In this letter we present a scaling formulation of the cluster size distribution in the case of irreversible aggregation of long-chain molecules, with one attractive functional group at each of the two ends of the chain. The irreversibility of the aggregation is relevant in the case when the binding energy is much greater than the thermal energy. For different chain lengths, but with a fixed concentration of monomers, we present a scaling ansatz for the number of clusters with l chains, at a given time t . We also carry out extensive numerical simulations in two dimensions for several different chain lengths and find that the results strongly support the scaling hypothesis.

Our starting point is the observation that the chain length N itself is a scaling variable if we study the N dependence in the formation of clusters. But the unit segment now is the chain length N and the mass would be discretised with N . Note that this discretisation does not occur for other scaling variables such as the number of stickers, reaction rate, temperature, and so on. For a moment, we restrict our discussion only to two scaling variables: the time t and the chain length N . We will later see the consequence of this discretisation in the generalised scaling description with many scaling variables.

In order to avoid the unnecessary discretisation, we define the size of the cluster, not by its mass but by the number of chains in the cluster. This way we remove the artificial discretisation in the cluster distribution function. Let $n_l(N, t)$ be the number of clusters per unit volume with l chains, at a given time t , for a system of N_T chains with N monomers in each chain. The concentration of the monomers, c , is fixed, i.e., $N_T N$ is a constant assuming that the volume of the system is fixed. We define $\langle l(N, t) \rangle$ as the average number of chains in a cluster at a given time t . When $t = 0$, there are only single clusters, whereas, for $t \rightarrow \infty$, only one cluster exists. Since for any finite time, $n_l(N, t)$ is expected to be a monotonically decreasing function of l , N , and t , we propose a time-dependent dynamic scaling form for $n_l(N, t)$ as:

$$n_l(N, t) = N^{-\alpha} t^{-\beta} l^{-\tau} G(l/\langle l(N, t) \rangle) \quad (1)$$

where the exponents α , β and τ are positive numbers. We also note that the total number of clusters in the system, given by $\sum_l n_l(N, t)$, is also a monotonically decreasing function of N and t . This quantity is expected to have a scaling form:

$$\sum_l n_l(N, t) \approx N^{-\omega} t^{-\delta}. \quad (2)$$

Thus, one finds that

$$\langle l(N, t) \rangle = \frac{\sum_i l n_i(N, t)}{\sum_i n_i(N, t)} \approx N^{\omega-1} t^\delta \quad (3)$$

valid over time range $t \ll t_x$, whereas, for $t \gg t_x$, $\langle l(N, t) \rangle \rightarrow N_T \approx N^{-1}$, and t_x defines the crossover time between these two functional behaviours. We also find from equation (1) that:

$$\sum_i n_i(N, t) = N^{-\alpha} t^{-\beta} \int dl l^{-\tau} G(l/\langle l(N, t) \rangle) \approx N^{-\alpha} t^{-\beta} \langle l(N, t) \rangle^{1-\tau}. \quad (4)$$

Thus, from equations (2) and (4), we find the following scaling relations:

$$\omega = \alpha - (\omega - 1)(1 - \tau) \quad \delta = \beta - \delta(1 - \tau).$$

Then it is a simple exercise to find that the scaling relation reduces to

$$n_i(N, t) = N^{-1} \langle l(N, t) \rangle^{-2} g(l/\langle l(N, t) \rangle) \quad (5)$$

where all the time dependency is now through the average cluster size $\langle l(N, t) \rangle$.

Note the appearance of a new factor N^{-1} in front of the scaling function. The novel feature of equation (5) is the realisation that any scaling variable that results in discretisation of mass would survive in the scaling function [14]. Such scaling variables, besides the chain length N , are the size of the monomer and the critical chain length in the dipole-dipole aggregation in the presence of a magnetic field[†]. On the other hand, scaling variables, such as temperature, reaction rate, or the number of stickers on the chain that do not result in discretisation of mass, would be absorbed through $\langle l \rangle$ and the resulting scaling function would have the same functional form obtained previously for the single particle aggregation [10].

In order to test the validity of our new scaling, we have carried out extensive numerical simulations on a two-dimensional square lattice of size 300×300 . We keep the concentration of the monomers fixed at 0.2 and consider chains with $N = 10, 20, 30$ and 40 monomer units in our study. In order to mimic the aggregation process of associative thickener molecules, we identify the two monomers at the two ends of the chains as the functional groups or sticker sites, and two chains can associate only when a sticker site of one chain is a nearest neighbour of a sticker site of the other chain during the aggregation process. Since the long-chain part of the associative thickener molecule is readily soluble in water, we consider the chains as self-avoiding walks which model polymers in good solvents quite accurately. As an initial configuration, we randomly place $N_T(N)$ chains of size N as self-avoiding walks of length $N - 1$ on the lattice. All the chains in the simulation are constructed to obey the excluded volume criterion, so that a lattice site cannot be occupied by more than one chain at any given instant of time. Thus, at $t = 0$, we have only single chain clusters. We mimic the dynamics of the flexible chains by *reptation* and by *wiggling*. During the time evolution, a chain is chosen randomly. Then, a reptation move towards one of the two directions along the chain, also chosen at random, is tried on that chain. In this move a vacant nearest-neighbour site of the first monomer (along the reptation

[†] If we start from the similar scaling ansatz for the mass distribution function, $n_s(N, t) = N^{-\alpha} t^{-\beta} s^{-\tau} F(s/S(t))$ with $S(t) = N^\omega t^\delta$, where s is the number of monomers in a cluster of l chains, then scaling with the mass conservation produces a scaling, $n_s(N, t) = s^{-2} G(s/S(t))$, which is compatible with equation (5), when we identify $n_l(N, t) = n_s(N, t) ds/dl = N n_s(N, t)$.

direction) moves all the way back to the end of the chain and the chain moves one step. A reptation step is accepted if the excluded volume criterion is satisfied, otherwise it is rejected. After the reptation trial, a wiggling move is tried on the same chain. In this process, a monomer is chosen randomly from the chain, and the details of the dynamics depend on whether this monomer is at any end of the chain or not. If this monomer is at the end of the chain, then a move is attempted to a randomly chosen nearest-neighbour site of its immediate neighbour along the chain, and the move is accepted if it complies with the excluded criterion. On the other hand, if the chosen monomer is not at an end of the chain, then the chain dynamics is simulated by using the Verdier-Stockmeyer algorithm [15]. If the location of this monomer is r_i , the new trial position r'_i is given by:

$$r'_i = r_{i+1} - r_i + r_{i-1}$$

where r_{i+1} and r_{i-1} are the locations of the $(i+1)$ th and $(i-1)$ th monomers respectively. The trial position r'_i is accepted only if it is not already occupied by any other chain molecule. One should note that the chain motion depends on the local conformation of the chosen monomer. In the simulation one time step is counted as one reptation trial *plus* one wiggling trial. In order to avoid the complexity arising from the chain aggregation process, we have employed an ideal version of the chain aggregation process based on a model for the single-particle aggregation [16]. In our model, which we call a *chain coalescence model*, the clusters are also defined to be *chains* with the same number of monomers as in the original chains. When two original chains happen to have any of their sticker sites as nearest neighbours, these two chains coalesce into a heavier single chain, which is counted as a cluster containing two chains. The configuration of this heavier chain is chosen randomly as the configuration of one of the two original chains. The dynamics of this heavier chain is simulated in the same way as the original chains. The process continues and clusters containing more and more chains appear in the system. We computed the cluster distribution function $n_i(N, t)$ at every 50 000 time steps for time up to $t = 500\,000$ and averaged the results over 10 different initial configurations for each value of N .

In figure 1 we plot our results for $\langle I(N, t) \rangle$ multiplied by $N^{0.4}$ against t . It seems clear that the data collapses on a single master curve for t up to 400 000 supporting

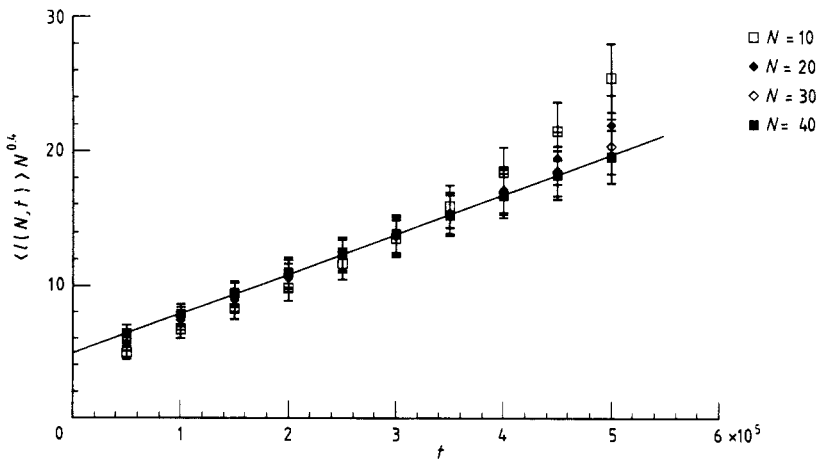


Figure 1. Plot of $\langle I(N, t) \rangle$ multiplied by $N^{0.4}$ against t for several N values. The straight line is the best fit to the data.

the scaling predictions over a broad time range. Also, we estimate the values of the scaling exponents ω and z , defined in equation (2) as $\omega = 0.6 \pm 0.2$ and $\delta = 1.0 \pm 0.2$, as shown in figure 1. This linear growth of the average number of chains in a cluster coincides with the prediction of the Smoluchowski equations [17]: if K is the constant aggregation rate in these kinetic equations, then the exact solution predicts $\langle l(N, t) \rangle \approx Kt$. This seems to imply that the mean-field description given by the Smoluchowski equation is a good representation of our data and that, for this system, $d = 2$ is above (or equal to) the upper critical dimension. A new feature here is the dependence on N of the kinetic coefficient K as $K \approx N^{\omega-1}$. The decreasing of the kinetic rate with N can be understood by noting that as N increases, it is more difficult for the stickers of different chains to meet with each other. Thus the slowing down with increasing chain length may be attributed to the reduced diffusion constant of the longer chains. The rate is also affected by the diffusive capture radius, which grows with molecular weight for flexible chains.

In order to study the new scaling hypothesis presented in equation (5), we plot $n_l(N, t)$ multiplied by N times $\langle l(N, t) \rangle^2$ against $l/\langle l(N, t) \rangle$ in figure 2 for several values of N and t . We find that all the data fall on a single curve suggesting that the new scaling prediction is well satisfied over the time range and values of N considered in the simulation. The data support an exponential decay for the scaling function which is again in agreement with the predictions of mean-field theory.

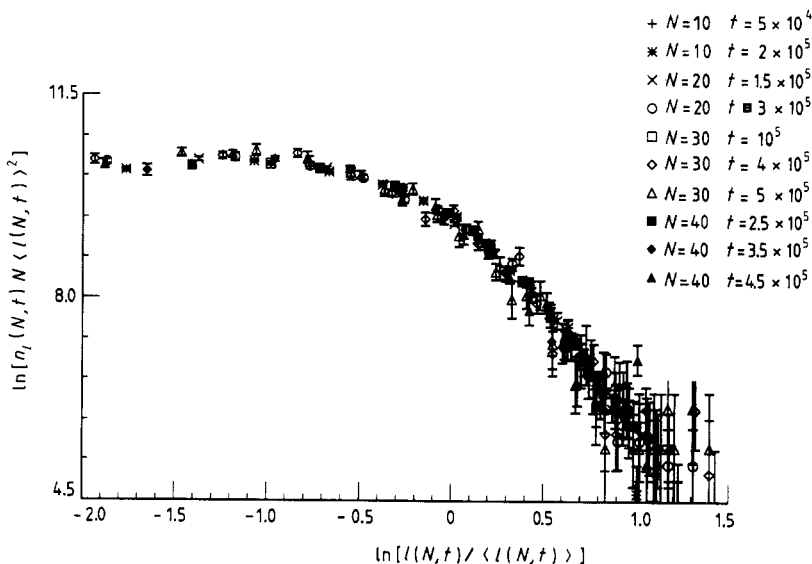


Figure 2. Scaling plot of $n_l(N, t)N\langle l(N, t) \rangle^2$ against $l/\langle l(N, t) \rangle$. The error bars are calculated from results for ten different random initial configurations for each value of N .

In summary, we have presented a scaling hypothesis for aggregation of long-chain molecules with sticker sites at both ends. We have demonstrated that any scaling variables that result in mass discretisation survive in the scaling function. We have carried out extensive numerical simulations to test the validity of these scaling ideas. Although the model considered by us in the numerical simulations contains some simplifying features and the simulations are carried out only in two dimensions due

to the limitations on the available computer time, the scaling form presented in this paper is expected to hold for any dimension. It would also be interesting to determine whether $d = 2$ is indeed the critical dimension (as in the case of single-particle aggregation) and what kind of correction one should expect to the scaling function and to the asymptotic growth law for the average number of chains in a cluster. These scaling ideas can be tested by light-scattering experiments on an aqueous solution of the associative thickener systems.

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