

## Kinetic growth of field-oriented chains in dipolar colloidal solutions

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Experimental studies on the irreversible growth of field-induced chains of dipolar particles suggest an asymptotic power-law behavior of several relevant quantities. We introduce a Monte Carlo model of chain growth that explicitly incorporates the anisotropic diffusion characteristic of a rodlike object. Assuming a simple power-law form for the mean cluster size  $S(t) \sim t^z$ , the results of our model are in good agreement with the experimental measurements of the dynamic exponent  $z$ . Nevertheless, an alternative scenario, including logarithmic corrections to the standard power-law behavior, provides a better and more insightful interpretation of the anomalous dynamic exponent. In contrast to some experimental findings, we do not observe any dependence of the exponents on the volume fraction of particles  $\phi$ . Finite-size effects are also explored by simulating very long time evolutions or highly concentrated systems. Two different behaviors are found, namely, saturation and a crossover to a quasi-one-dimensional regime. [S1063-651X(99)08201-X]

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### I. INTRODUCTION

The kinetic properties of the irreversible aggregation of particles has been the subject of great interest over the past decade [1–3]. In particular, several experimental and theoretical studies as well as computer simulations have been devoted to understanding the behavior of colloidal suspensions of dipolar particles, the so-called *electrorheological* and *magnetorheological fluids* [4–11]. After applying an external electric or magnetic field, these suspensions experience a dramatic change in their rheological properties, i.e., a notable increase in the viscosity, which renders them particularly interesting systems from a technological point of view.

The change in the rheological properties of dipolar suspensions upon the action of an external field is mainly due to the aggregation of the colloidal particles, which form clusters of macroscopic size. These are usually linear chains, rods, oriented along the direction of the applied field, although for high enough concentrations of dipolar particles more complex structures may arise [12,13]. The overall spatial arrangement of the aggregates is very effective in hindering the fluid flow, conferring the suspension a solidlike texture.

Multiple applications have been envisaged for these materials: lubricants, dampers, heat and light transmission devices, etc. Nevertheless, their eventual manufacture still has to overcome different drawbacks, for instance, the sedimentation of the clusters. At high fields, the aggregation is irreversible; the chains grow longer and never break as long as the field is present. Thus the study of the kinetics of formation of the aggregates turns out to be an issue of practical importance.

Due to its irreversible character, studies have most often focused on the dynamic properties of the distribution of clusters, following the approach developed to deal with irreversible cluster-cluster aggregation models (see Refs. [2,3] and references therein). Within this framework, the quantitative features of the aggregation are commonly described in terms of the *cluster-size distribution* as a function of time  $n_s(t)$ , which is defined as the number of clusters of size  $s$ , per unit

volume, present in the system at time  $t$ . Other relevant quantities are the density of clusters at time  $t$ ,  $n(t) = \sum_s n_s(t)$ , and the *mean cluster size*  $S(t)$ , defined by

$$S(t) = \frac{\sum_s s^2 n_s(t)}{\sum_s s n_s(t)}. \quad (1.1)$$

Experimental results and computer simulations of different cluster-cluster aggregation models [2,3] show that the asymptotic behavior at large times of the mean cluster size and the total number of clusters is a power law

$$S(t) \sim t^z, \quad n(t) \sim t^{-z}. \quad (1.2)$$

The exponent  $z$  is the so-called *dynamic exponent*. In general,  $z$  depends on the dimension  $d$  of the space as well as on the nature of the aggregation process. Another relevant feature of the aggregation dynamics is that the characteristic quantities defined above are related through the *dynamic scaling hypothesis* [14]

$$n_s(t) = s^{-2} F(s/S(t)), \quad (1.3)$$

where  $F(x)$  is a certain scaling function, independent of  $t$  and  $s$ . The validity of this relation has been systematically verified in experiments and computer simulations.

The dynamics of cluster-cluster aggregation can be theoretically described in terms of the Smoluchowski equation [15]. Smoluchowski proposed a kinetic equation describing the temporal evolution of the cluster-size distribution  $n_s(t)$ :

$$\frac{dn_s(t)}{dt} = \sum_{i+j=s} K(i,j)n_i(t)n_j(t) - n_s(t) \sum_{i=1}^{\infty} K(s,i)n_i(t). \quad (1.4)$$

Here  $K(s,s')$  is the reaction kernel, giving the rate at which clusters of size  $s$  join clusters of size  $s'$  to form clusters of

size  $s + s'$ . This equation is an example of a mean-field-type theory in which fluctuations are neglected. Moreover, its range of applicability is limited to low concentrations, where the assumption of exclusively binary collisions is valid [15]. The results of this theory are expected to hold for dimensions higher than the *upper critical dimension* ( $d_c = 2$  in this case [16]), above which fluctuations become irrelevant. Assuming that the reaction kernel is a homogeneous function of degree  $\gamma$ , that is,

$$K(bs, bs') \equiv b^\gamma K(s, s'), \quad (1.5)$$

it is possible to prove the relations (1.2) and (1.3) [3], with a dynamic exponent given by

$$z = \frac{1}{1 - \gamma}. \quad (1.6)$$

Most of the experimental and numerical studies of the anisotropic aggregation of *rodlike clusters* presented so far [5,7,8,10,17] seem to indicate the same type of power law for the asymptotic behavior of the mean cluster size  $S(t)$ . For instance, Fraden *et al.* [5] reported a value of  $z = 0.60$ . Promislow and Gast [8], on the other hand, measured a value of  $z$  ranging between 0.50 and 0.75 for different values of the concentration and the dipolar interaction strength  $\lambda$  (to be defined later on). The interpretation of these results relies on Smoluchowski's assumptions.

In Smoluchowski's solution [15], the reaction kernel is the product of an effective diameter, the collision cross section of two clusters ( $R_s + R_{s'}$ ), times an effective relative diffusion coefficient [ $D(s) + D(s')$ ], where  $R_s$  and  $D(s)$  are the radius of influence and the diffusion coefficient of a cluster of mass  $s$ , respectively [18]. By analogy with the Stokes-Einstein relation for a single spherical particle of diameter  $a$  moving in a liquid  $D \propto a^{-1}$  [19], the effective diffusion coefficient is given by a power law of the cluster size

$$D(s) \sim s^\gamma. \quad (1.7)$$

Miyazima *et al.* [10] proposed this type of power-law kernel for rodlike clusters of dipolar particles. One can estimate the effective cross section, the radius of influence, of a single magnetic particle  $R_1$  by comparing dipolar [ $U_d(r) \propto m^2/r^3$ ] and thermal ( $k_B T$ ) energies. If we introduce the dimensionless parameter  $\lambda = m^2/a^3 k_B T$ , where  $m$  is the magnetic moment and  $a$  the diameter of a dipolar particle, the effective cross section can be expressed as  $R_1/a \sim \lambda^{1/3}$ . The detailed form of the dipolar interaction is not expected to modify the asymptotic behavior of the aggregation dynamics. Thus, roughly speaking, outside a spherical region of radius  $R_1$  the relative motion is mainly diffusive and only when one particle enters the sphere of influence of another do they stick irreversibly.

At low concentrations, it is reasonable to assume that rodlike clusters of dipolar particles essentially aggregate tip to tip. Miyazima *et al.* argued that, under such conditions, the cross section of a chain cannot depend on its total length [20] and it is possible to approximate  $R_s \sim R_1$ . The only source of dependence on the cluster size should thus come from the effective diffusion coefficient and the reaction kernel is approximately given by  $K(s, s') \sim s^\gamma + s'^\gamma$ . This form fulfills

the homogeneity condition (1.5) and yields therefore a dynamic exponent given by Eq. (1.6).

Following this approach to the problem, the value of  $\gamma$  is the key parameter in order to interpret the experimental data [5,7,8]. The dynamic exponent  $z$  is numerically computed from a log-log plot of the mean chain length  $S(t)$  as a function of time. The value obtained is then associated through Eq. (1.6) with a particular value of  $\gamma$ . In the absence of hydrodynamic interactions among the spheres in a chain, the effective mobility is inversely proportional to its length. Consequently, one would expect  $\gamma$  to be equal to  $-1$  which, according to Eq. (1.6), corresponds to  $z = 1/2$ . In general, this value of  $z$  deviates from the ones measured experimentally. A simple way of interpreting this difference is to consider an *ad hoc* value of  $\gamma$  different from  $-1$ , which phenomenologically accounts for a more realistic mobility of a rodlike particle [21].

In this paper we propose an alternative mechanism to explain those discrepancies in the measured value of  $z$ . The core of our proposal is a different view of the mobility of a cluster of mass  $s$ . Fraden *et al.* [5] already pointed out that hydrodynamic interactions should *increase* the effective mobility of a cluster of mass  $s$ , making it larger than the mobility of a collection of  $s$  independent particles. The latter approximation, stating  $D(s) \sim s^{-1}$ , is strictly valid for clusters of *hydrodynamically noninteracting* spheres [22]. However, this is too strong an assumption in the case under consideration, where the magnetic spheres form relatively rigid chains. In this case, it is well known that the hydrodynamic drag for the translational motion is *anisotropic* [21,23]. The drag coefficients along the direction parallel to the axis of the chain and in the perpendicular directions  $\xi_{\parallel}$  and  $\xi_{\perp}$ , respectively, are approximately given by [23]

$$\xi_{\parallel} = 2\pi\eta a \frac{s}{\ln(s)}, \quad \xi_{\perp} = 2\xi_{\parallel}, \quad (1.8)$$

where  $\eta$  is the viscosity of the solvent and  $s$  is the number of particles composing the cluster, its mass. The mobility of a cluster is defined as the inverse of the drag coefficient; hence the constants  $D_{\parallel}$  and  $D_{\perp}$ , characterizing the diffusion parallel and perpendicular to the rods' axis, are given by [18]

$$D_{\parallel} = \frac{k_B T}{\xi_{\parallel}} \sim \frac{\ln(s)}{s}, \quad D_{\perp} = \frac{k_B T}{\xi_{\perp}} = \frac{D_{\parallel}}{2}. \quad (1.9)$$

That is to say, hydrodynamic interactions generate anisotropic diffusion coefficients, exhibiting logarithmic corrections to the previously considered power laws. In order to investigate the effect of the new diffusivities (1.9) on the dynamics of the process, we have introduced them in a Monte Carlo [24] computer model for the cluster-cluster aggregation of rodlike particles.

By simply considering anisotropic diffusivities with logarithmic corrections and assuming that  $S(t) \sim t^z$ , we are able to recover a dynamic exponent  $z$  in good agreement with experimental results. However, a simple heuristic argument suggests a different functional form, namely, a power law with logarithmic corrections.

Let us assume that all clusters in the suspension have the same average length  $S$ . The average separation  $\bar{R}$  between

neighboring clusters in a suspension with initial volume fraction  $\phi$ , the initial density of dipoles, can then be estimated to be

$$\bar{R} \approx \left( \frac{S}{\phi} \right)^{1/d}. \quad (1.10)$$

In  $d=1$ , only two neighboring clusters are able to aggregate. In general, this is the most likely event in low dimensions. In high dimensions, however, and due to the diffusive nature of their movement, any two clusters are equally likely to join, irrespective of their relative distance, as they are quite invisible to each other. A mean-field type of behavior is thus expected, in the sense that only the density of clusters present  $n(t)$  is relevant and not their spatial arrangement.

As the movement of the clusters is essentially diffusive, the average displacement of a cluster of mean size  $S$  after the time interval  $t$  is given by

$$\langle R^2 \rangle \propto D(S)t, \quad (1.11)$$

where, as indicated in Eq. (1.9),  $D(S) \sim \ln(S)/S$ . Aggregation of two clusters will occur after a characteristic time  $T$  has been elapsed, a time interval long enough for the clusters to cover their relative separation.

For a low-dimensional system, the characteristic time  $T$  is that required to cover the distance  $\bar{R}$  separating near neighbors, i.e.,

$$T \propto \frac{\bar{R}^2}{D(S)} \propto \frac{1}{\phi^{2/d}} \frac{S^{(2+d)/d}}{\ln(S)}. \quad (1.12)$$

On the other hand, in higher dimensions there is no such characteristic length scale and, consequently, there is no reason to expect that the previous expression holds. However, we can argue that a cluster browsing a volume of order unity will encounter  $n(t)$  clusters available to join. The time needed for a cluster to cover such space will be thus proportional to  $nT$ , where, as above,  $T$  is the characteristic time of a *single* aggregation event. We have then

$$T \propto \frac{1}{n} \frac{1}{D(S)} \propto \frac{1}{\phi} \frac{S^2}{\ln(S)}, \quad (1.13)$$

where we have used that  $n \sim \phi/S$ . Note that both estimations yield the same result at  $d=2$ , suggesting that the upper critical dimension of the problem is  $d_c=2$  [16].

The inspection of Eqs. (1.12) and (1.13) suggests that the functional dependence of the mean cluster size with time takes the form, for  $d \leq d_c$ ,

$$\frac{S}{[\ln(S)]^\zeta} \sim (t\phi^{2d})^\xi, \quad (1.14)$$

where  $\zeta = d/(2+d)$ , and for  $d \geq d_c$ ,

$$\frac{S}{[\ln(S)]^{1/2}} \sim (t\phi)^{1/2}. \quad (1.15)$$

Note that within this approach, we obtain logarithmic corrections to the behavior reported in Ref. [10] for  $\gamma = -1$  [see

Eq. (1.6)]. These corrections to the usual asymptotic behavior in *isotropic* cluster-cluster aggregation could explain the anomalous dynamic exponent found for the aggregation of anisotropic rodlike clusters. The results of our numerical simulations exhibit a surprisingly good fit to the theoretical predictions (1.14) and (1.15), better than to the naive power-law behavior.

We have structured our paper as follows. In Sec. II we describe the technical details of our algorithm. Section III deals with the properties of rodlike aggregation in two dimensions. In particular, we study the mean cluster size  $S(t)$  for a variety of values of the initial volume fraction  $\phi$ . For small to moderate values of  $\phi$  and not very long execution times, we recover, assuming a pure power-law form for  $S(t)$ , values of  $z$  in agreement with some of the experimental findings. Importantly, in opposition to some claims in the literature [8], we do not observe any dependence of  $z$  on the volume fraction. On the other hand, we observe that the same sets of data can be fitted with higher accuracy to our predicted power law with logarithmic corrections. By allowing very high volume fractions or large execution times, we find that our model crosses over to two different behaviors, namely, saturation and a quasi-one-dimensional regime. We believe that the discrepancies with the experimental results in Ref. [8] might be due to a combination of these types of finite-size effects and logarithmic corrections. In Sec. IV we extend our model to three dimensions. We do not observe significant variations with respect to the two-dimensional aggregation. Finally, our conclusions are presented in Sec. V.

## II. COMPUTER MODEL

In our model we consider the irreversible aggregation of rigid rodlike clusters in  $\mathbb{R}^d$ , with  $d=2$  and 3. Clusters are oriented along the  $Z$  axis. Simulations start at  $t=0$  with a random distribution of  $N_0$  monomers (spherical particles of diameter  $a=1$ ) in a box of volume  $V$  with periodic boundary conditions. The initial volume fraction of monomers is defined by  $\phi = N_0/V$ . We have simulated a wide range of volume fractions  $\phi$  (0.001–0.1) and some particular high values (up to 0.5). Clusters diffuse performing a free off-lattice random walk; that is, despite the dipolar interactions, we assume that the temperature in the system is high enough to provide a mainly diffusive character to the aggregation dynamics. Nevertheless, dipolar interactions are predominant at short distances. Therefore, when two clusters come close enough to each other, they stick irreversibly.

In the Monte Carlo algorithm, clusters are selected and moved a distance equal to one diameter  $a$  in a direction chosen randomly from a certain probability distribution. The movement is performed rigidly, preserving the orientation of the rod along the  $Z$  axis. When two clusters come within a distance tip to tip of one diameter (that is, when the distance between any two of their respective ends is less than or equal to  $a$ ) they join, forming one single rod of mass, number of particles, equal to the sum of the masses of the colliding clusters. When two clusters approach side to side they repel each other. This is implemented by rejecting all possible movements leading to a side to side overlap of clusters.

In fact, this procedure is equivalent to considering a radius of influence  $R_s = a$  and, according to the discussion in

Sec. I, it mimics a dipolar interaction of strength  $\lambda \sim 1$ . Different values of  $\lambda$  could be in principle simulated by joining clusters irreversibly when they come within a distance  $\sim \lambda^{1/3}$ . Values of  $\lambda$  between 1 and 30 (that is, radius of influence between 1 and 3), within the range reported in experimental investigations, provide analogous asymptotic results at large times, differing only in the transient regimes.

The effect of the anisotropic diffusivities (1.9) on the algorithm is taken into account in two steps: first, in the selection of the next cluster to be moved, and second, in the prescription for the direction of its tentative movement. In the first step, we choose a cluster among all present at a given time step, with a probability  $\rho(s)$  proportional to their diffusivity. According to Eq. (1.9) we have

$$\rho(s) \sim \frac{\ln(s)}{s}. \quad (2.1)$$

However, given that the expression (1.9) is only suitable to describe the motion of a *slender* body ( $s \gg 1$ ), the previous expression would be inappropriate for small  $s$ . Therefore, we actually select the cluster with a probability proportional to the corrected diffusivity

$$\rho(s) \sim \tilde{D}_C(s) = \begin{cases} \ln(s_0)/s & \text{for } s < s_0 \\ \ln(s)/s & \text{for } s \geq s_0. \end{cases} \quad (2.2)$$

Here we are assuming that small clusters ( $s < s_0$ ) diffuse as if composed of hydrodynamically independent particles. We have selected a cutoff mass  $s_0 = 3$ ; different values were also tested, yielding comparable results.

We discuss now the method employed to sample the clusters. In cluster-cluster aggregation simulations, the sampling with a probability proportional to the mobility is usually performed according to the ‘‘rejection’’ algorithm (see [2,25] and Ref. [26], p. 151): A cluster is selected among all the present at a given time, with uniform probability. Then a random number  $\eta$ , uniform in the interval  $[0,1]$ , is drawn. The cluster selected is accepted for movement if  $\eta < D(s)/D_{\max}$ , where  $D(s)$  is the diffusion coefficient of the cluster considered and  $D_{\max}$  is the maximum diffusivity of all the clusters present. Otherwise, the cluster is rejected and both selection steps are repeated. In our simulations, however, we have chosen to implement a different sampling algorithm, the ‘‘alias’’ method for discrete distributions (see Ref. [26], p. 158, for a detailed description). Briefly, the algorithm works as follows. A cluster  $C$ , of size  $s$ , is selected uniformly among all clusters. Then, with a certain ‘‘aliasing’’ probability  $p(s)$ , the cluster is replaced by its alias  $C' = \mathcal{F}[C]$ , of mass  $s'$ . The probability  $p(s)$  is chosen so that clusters with small  $\tilde{D}_C(s)$  (low probability of being selected) are frequently mapped to clusters with higher  $\tilde{D}_C(s')$ . The alias method is more costly in computer time; however, it provides a more accurate sampling of the probability density  $\rho(s)$ .

With the procedure described above, we implement the mass dependence of the mobility (1.9). However, we also have to take into account its *anisotropy*. Given Eq. (1.9), it is twice more likely for any rod to move along its axis than along any other perpendicular direction. We implement this fact in a second step by selecting the direction of the trial

movement from a probability distribution fulfilling this same anisotropy. Let us define the azimuthal angle  $\theta$  with respect to the axis of the rod. Then, in  $d=2$ , the direction for the tentative movement of a chain of length  $s \geq s_0$  is selected at random from the probability density

$$P(\theta) = \frac{\sqrt{2}}{2\pi} \frac{1}{1 + \sin^2 \theta}, \quad (2.3)$$

with  $0 < \theta < 2\pi$ . In  $d=3$  we use instead the density

$$P(\varphi, \theta) = \frac{1}{2\pi} \frac{\sqrt{2}}{\ln(3 + 2\sqrt{2})} \frac{1}{1 + \sin^2 \theta}, \quad (2.4)$$

with  $0 < \varphi < 2\pi$  and  $0 < \theta < \pi$ . These distributions ensure the necessary anisotropic condition  $P[\theta=0, \pi]/P[\theta = \pi/2, 3\pi/2] = 2$ , while being continuous in both angles and easily simulated numerically. For clusters of mass  $s < s_0$  we assume that the diffusion is isotropic. Therefore, in this case we choose a random direction for the tentative movement from a uniform distribution.

The final implementation of our algorithm runs as follows. (i) Each time step we select at random a cluster of mass  $s_i$  according to the probability density (2.2) and a direction  $\theta_i$ , according to Eq. (2.3) [a pair  $(\theta_i, \varphi_i)$ , according to Eq. (2.4), in three dimensions] for  $s_i \geq s_0$ ; in the case that  $s_i < s_0$ , the direction is drawn from a uniform distribution. (ii) The cluster is moved a distance  $a$  in the selected direction and its position with respect to the neighboring chains is analyzed. (iii) If it intersects side to side with another chain, the movement is rejected; otherwise, it is accepted. If the cluster intersects tip to tip with another chain, they join and form a single cluster. (iv) Finally, the time is incremented by an amount

$$\Delta t = \frac{1}{N(t)\tilde{D}_C(s_i)}, \quad (2.5)$$

where  $N(t)$  is the total number of clusters present at the corresponding time  $t$  and  $\tilde{D}_C(s_i)$  is the effective diffusivity of the selected cluster, as given by Eq. (2.2). This choice of the time step effectively reproduces the real dynamics of the system.

### III. AGGREGATION IN $d=2$

In our simulations in  $d=2$  we have mainly considered systems with volume ranging from  $256 \times 128$  to  $1024 \times 512$  and initial number of particles between 524 and 67 109. This corresponds to volume fractions ranging between  $\phi \sim 0.001$  and  $\phi \sim 0.1$ . We have also considered the extreme case of high concentration ( $\phi \sim 0.5$ ) in order to investigate a possible crossover to a one-dimensional regime. In most cases, averages were performed over 100–500 simulations.

#### A. Isotropic diffusion

First, in order to check our algorithm, we have simulated the aggregation according to the prescription given in Ref. [10], i.e., the diffusivity of a rod is isotropic and inversely proportional to its mass  $D(s) \sim s^{-1}$ . In Fig. 1(a) we repre-

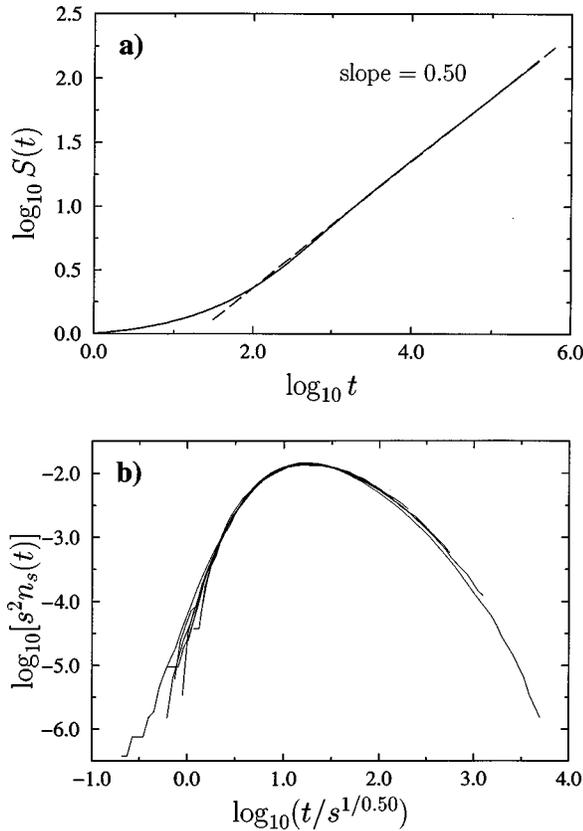


FIG. 1. Aggregation with cluster diffusion that is isotropic and proportional to  $s^{-1}$ . The initial concentration  $\phi=0.019$ . (a) Mean cluster size as a function of time. (b) Finite-size scaling of the cluster size distribution as a function of time, for fixed lengths  $s = 10, 20, 30, 40, 50, 60, 70$ , and  $80$ .

sent the mean cluster size  $S(t)$  obtained from simulations of a system of size  $1024 \times 512$ , with an initial number of particles  $N_0 = 10\,000$ . These values correspond to an initial volume fraction  $\phi = 0.019$ . We observed a clear power-law regime covering more than three decades in time. The least-squares fitting of the curve yields an exponent  $z = 0.50$ . As expected, this result matches the dynamic exponent predicted by Eq. (1.6) for  $\gamma = -1$ . In Fig. 1(b) we have tested the finite-size scaling relationship (1.3) by plotting  $s^2 n_s(t)$  as a function of the rescaled time  $t/s^{1/z}$  for different values of the cluster size  $s$ . The best collapse of the plots is obtained for a value of  $z = 0.50$ , which is again in agreement with Eq. (1.6).

### B. Anisotropic diffusion: Dilute regime

We now discuss the results obtained by implementing into our algorithm the anisotropic diffusion prescribed in  $d=2$  by Eqs. (2.2) and (2.3). First of all, motivated by the results in Ref. [5], we have duplicated the parameters in that experiment, i.e., we have chosen a system of volume  $1024 \times 512$  and an initial number of particles  $N_0 = 5000$ . These conditions yield a volume fraction  $\phi \sim 0.01$ , as in the experiments. Figure 2(a) shows the mean cluster size as a function of time, in a double-logarithmic plot. The behavior of  $S(t)$  at late times can be fitted to a power law extending close to three orders of magnitude. A least-squares fitting provides an exponent  $z = 0.61$ , in complete agreement with the experimental findings in [5]. Similarly, in Fig. 2(b) we represent the

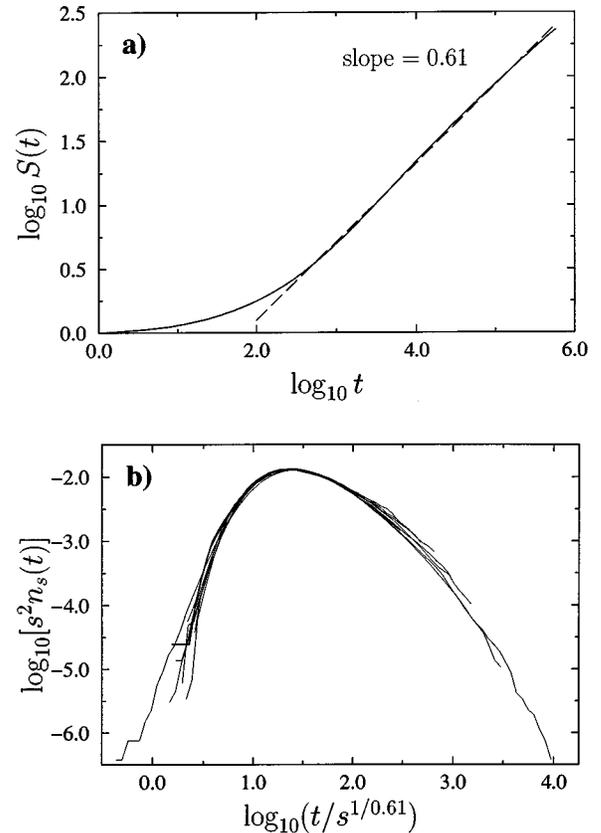


FIG. 2. Aggregation with cluster diffusion that is anisotropic and proportional to  $\ln(s)/s$ , as defined in Eqs. (2.2) and (2.3). The initial concentration  $\phi = 0.009$ , as in Ref. [5]. (a) Mean cluster size as a function of time. (b) Finite-size scaling of the cluster size distribution as a function of time, for fixed lengths  $s = 10, 20, 30, 40, 50, 60, 70$ , and  $80$ .

finite-size scaling hypothesis (1.3). The good collapse shown in this plot corroborates the value of the dynamic exponent  $z = 0.61$ .

The evidence exposed in the previous figures seems to lend support to the hypothesis of a simple power-law behavior. However, the situation is not completely clear, as we show in Fig. 3. Figure 3(a) tests the theoretical prediction (1.14). Plotting  $S(t)$  as a function of  $t \ln S$  in logarithmic scale we obtain a slope  $\zeta = 0.51$ , very close to the expected value  $1/2$  in  $d=2$ . Moreover, we remark that the goodness of fit in this case, as measured by the Pearson  $r$  coefficient [27], is higher than the one obtained from the linear regression in Fig. 2(a). Indeed, least-squares fittings covering the last three orders of magnitude in the abscissas of Figs. 2(a) and 3(a), yield the values  $r = 0.999\,60$  and  $r = 0.999\,948$ , respectively. In Fig. 3(b) we check the finite-size scaling hypothesis by plotting  $s^2 n_s(t)$  as a function of the rescaled time  $t \ln s^{1/\zeta}$ . The best collapse again results from a value of  $\zeta = 0.51$ .

In the simulations presented above we have been able to match the observed value of  $z$  by selecting the particular value of  $\phi$  reported in the experiments. It has been argued, however, that the value of  $z$  may depend on the volume fraction  $\phi$  [8]. In order to verify the accuracy of this statement, we have performed simulations for several values of  $\phi$ , ranging from very dilute ( $\phi = 0.001$ ) to moderate concentrations ( $\phi = 0.1$ ), in a system of fixed size  $1024 \times 512$ . Fig-

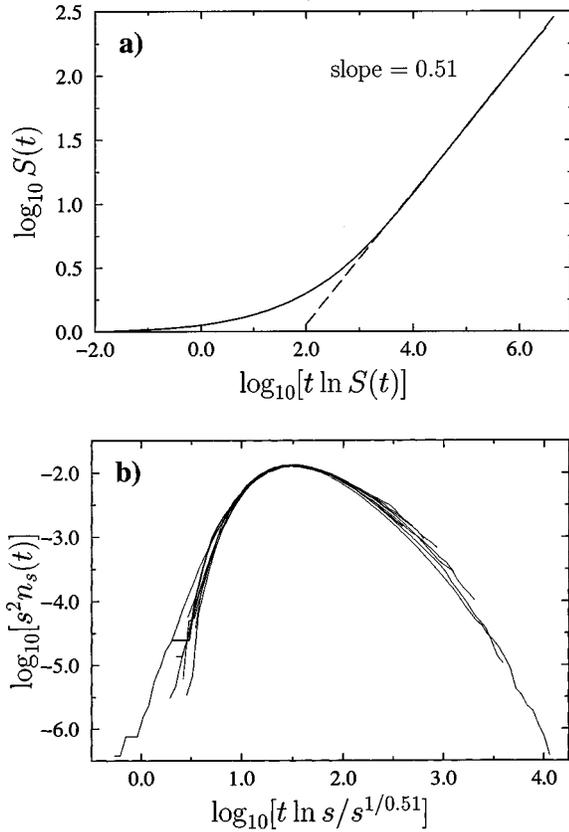


FIG. 3. Same data as in Fig. 2. (a) Mean cluster size as a function of  $t \ln S(t)$ . (b) Finite-size scaling of the cluster size distribution.

ure 4(a) plots the mean cluster size  $S(t)$  as a function of  $t$  for the different volume fractions considered. The slope of the different graphs depicted in this figure does not seem to depend on  $\phi$ . This fact becomes even more clear in Fig. 4(b), where we have plotted  $S(t)$  as a function of the *rescaled time*  $\phi t$ . We observe that in this case all the plots *collapse* onto a universal function, independent of the volume fraction. The collapse of the different graphs is also shown in Fig. 5, now as a function of the rescaled quantity  $\phi t \ln S$ . Note that Eq. (1.14) leads directly to the required scaling factor of  $\phi$  in  $d=2$ . As in Fig. 3, the collapse is statistically better in terms of this new rescaling than for the single power law.

The collapsed plots allow us to select a common scaling region for all of them, from which we can extract slopes for the different values of  $\phi$  that are directly comparable. An average slope can thus be defined. In the case of Fig. 4(b) (single power-law interpretation), individual slopes range between 0.59 and 0.63. From them we obtain an average exponent  $z=0.61$ , in accordance with our previous estimate and the experimental results in Ref. [5]. In addition, from Fig. 5 (power law with logarithmic corrections) we obtain slopes between 0.49 and 0.53, yielding an average value of  $\zeta=0.51$ .

### C. Anisotropic diffusion: Saturated regime

In view of the results presented in the preceding subsection, we naturally conclude that the slope does not depend on the volume fraction and that the disagreement with prior ex-

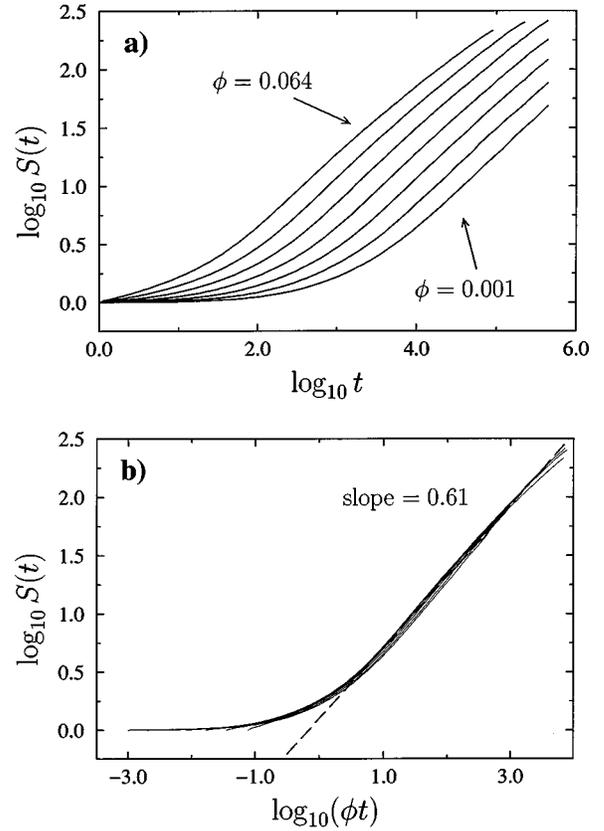


FIG. 4. Mean cluster size for anisotropic aggregation, for several values of the volume fraction. From top to bottom,  $\phi=0.064$ , 0.032, 0.016, 0.008, 0.004, 0.002, and 0.001. (a) As a function of time. (b) As a function of the rescaled time  $\phi t$ . The average slope obtained from the common scaling region is  $z=0.61$ .

perimental findings [8] may be a consequence of both logarithmic corrections and finite-size effects. In experiments or computer simulations, finite-size effects can cause the system to crossover, at large times, to a *saturated* regime in which any predicted scaling behavior is lost. We have investigated this issue by simulating systems that were allowed to evolve for very long times, up to ten times longer than in our previous simulations. Figure 6 depicts the mean cluster size computed for different system sizes, while keeping the same

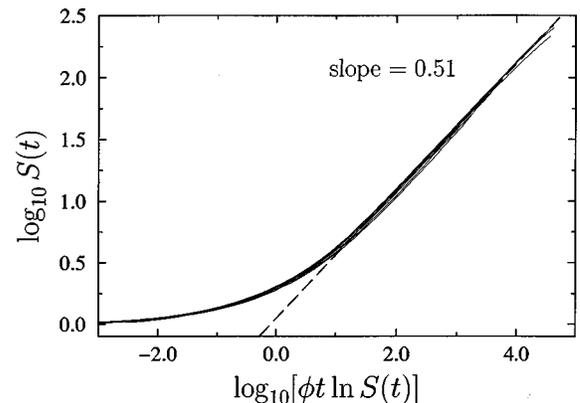


FIG. 5. Same data as in Fig. 4, but now as a function of the rescaled quantity  $\phi t \ln S$ . The average slope obtained from the common scaling region is  $\zeta=0.51$ .

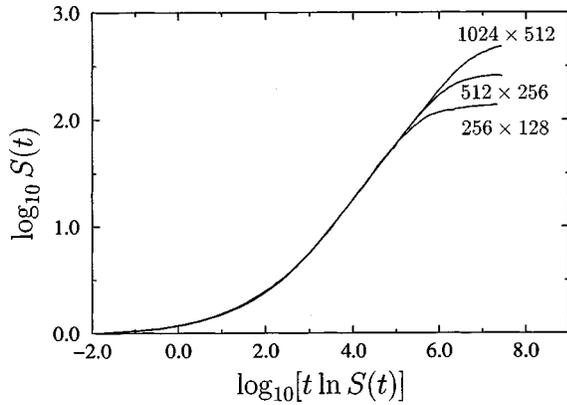


FIG. 6. Mean cluster size as a function of  $t \ln S(t)$ , for anisotropic aggregation in the saturated regime. The plots correspond to a fixed volume fraction  $\phi=0.019$  and different system sizes. The onset of the plateau and its height are functions of the system volume.

fixed initial volume fraction  $\phi=0.019$ . In Fig. 7 we plot  $S(t)$  for a fixed value of the system size  $512 \times 256$  and different values of  $\phi$ . The chief feature of these plots is the onset of a plateau whose location and height appears to be a function of the system volume  $V$ . This flatter region is indicative of a considerable slowing down in the dynamics. Finite-size effects, unavoidable at relatively large times, can corrupt the interpretation of any expected scaling behavior.

#### D. Anisotropic diffusion: Quasi-one-dimensional regime

We have established the existence of deviations from the dilute asymptotic behavior due to saturation when the system evolves up to very long times. In addition, in a highly concentrated system, one can also observe a crossover to a *quasi-one-dimensional regime*, as remarked by Miyazima *et al.* [10]. At the late stages of evolution in a very concentrated system, the largest chains attain a length that is of the order of the system size. Their effect is therefore to divide the plane into one-dimensional strips. The aggregation of the

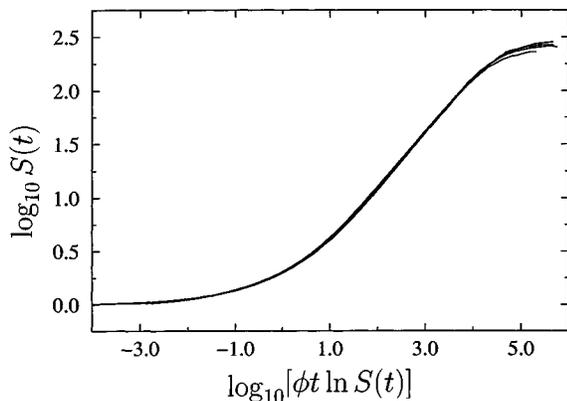


FIG. 7. Mean cluster size as a function of the rescaled quantity  $\phi t \ln S(t)$ , for anisotropic aggregation in the saturated regime. The plots correspond to a fixed system size  $512 \times 256$  and different volume fractions  $\phi=0.0048, 0.0095, 0.0191$ , and  $0.038$ . The collapse of the curves shows that both the onset and the height of the saturated plateau depend only on the system size.

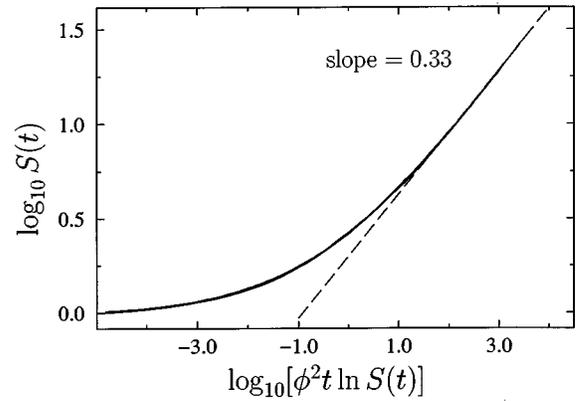


FIG. 8. Mean cluster size as a function of the rescaled quantity  $\phi^2 t \ln S(t)$ , for anisotropic aggregation in  $d=1$ . The plots correspond to a fixed system size 10 000 and different volume fractions  $\phi=0.02, 0.03$ , and  $0.04$ . The average slope obtained from the common scaling region is  $\zeta=0.33$ .

remaining smaller clusters is thus mainly restricted to occur within these strips [5], becoming effectively a one-dimensional process.

In a truly one-dimensional model of aggregation, according to Eq. (1.14), we expect the mean cluster size to satisfy  $S(t) \sim [\phi^2 t \ln S(t)]^{1/3}$ . For the sake of completeness, we have adapted our model to simulate aggregation within a line. The only relevant change in the algorithm concerns the way in which the direction of the tentative movements is selected: either to the right or to the left, with equal probability. The results of the simulations are plotted in Fig. 8. This figure corroborates both the correct scaling of time with  $\phi^2$  (in contrast to  $\phi$  for  $d \geq 2$ ) and an exponent  $\zeta=0.33$ .

We next present results from simulations in  $d=2$  of a system exhibiting quasi-one-dimensional behavior. The data in Fig. 9 correspond to a volume fraction  $\phi=0.48$  in a system of volume  $1024 \times 512$  [28]. After a transient regime, we observe that the slope stabilizes in a value  $\zeta \approx 0.32$ , clearly smaller than the one found for less concentrated systems and in excellent agreement with the exponent  $\zeta=1/3$  expected in  $d=1$ . We note that both the slope and the crossover time do not depend on the volume of the system for a fixed value of

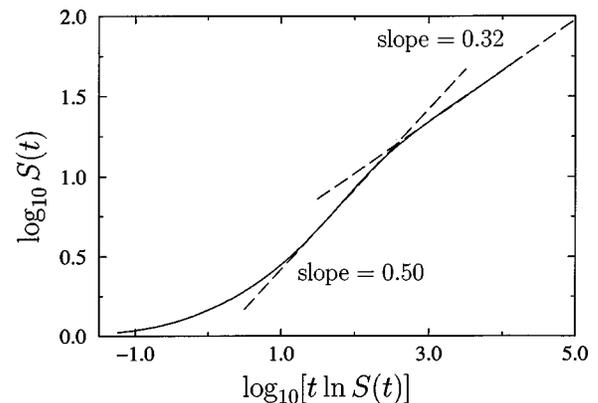


FIG. 9. Mean cluster size as a function of  $t \ln S(t)$ , for anisotropic aggregation in  $d=2$ , in the quasi-one-dimensional regime. The dashed lines have slopes  $\zeta=0.32$  at larger times and  $0.50$  at intermediate times, corresponding to the asymptotic dilute regime.

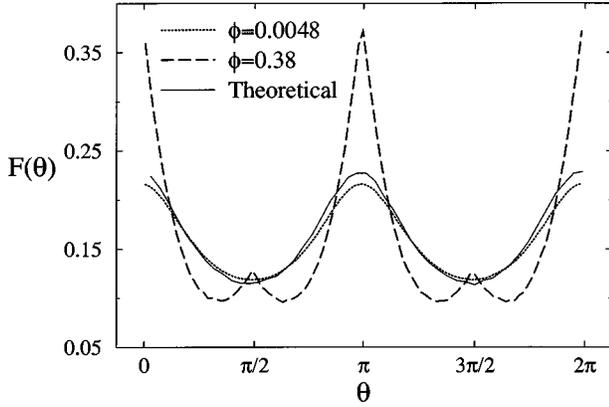


FIG. 10. Jump orientation density  $F(\theta)$  for two systems of size  $512 \times 256$ , at two different volume fractions. The dilute system ( $\phi=0.0048$ ) matches the *a priori* angle distribution (2.3) (full line). The concentrated system ( $\phi=0.38$ ), in the quasi-one-dimensional regime, shows two sharp peaks at  $\theta=0$  and  $\theta=\pi$ .

$\phi$ . The results obtained from simulations in a volume  $512 \times 256$  (not shown) confirm this statement.

We have further investigated the difference between the saturated and the quasi-one-dimensional regimes. An effective way of doing so is to consider the movement of the individual clusters. As discussed above, in the quasi-one-dimensional regime, average-sized clusters are confined to move within the narrow strips delimited by the largest chains. Therefore, it is more likely for a cluster to move along the direction parallel to the  $Z$  axis than in any other direction perpendicular to it. This effect can be quantitatively assessed by estimating the relative frequency with which clusters move in a given direction  $\theta$ . To this end, we define the *jump orientation density*  $F(\theta)$  as follows: At the last stages of the simulations (usually the last 25% of the time allotted for the run) we keep track of the direction  $\theta$  of all the *accepted* movements performed by the clusters.  $F(\theta)d\theta$  is then defined as the probability that any of those movements is directed along a direction included in the interval  $[\theta, \theta + d\theta]$ . At late times in the evolution of the system, most of the clusters have a length larger than the cutoff  $s_0$ . If there is no bias in the direction taken by the accepted steps, we expect that the function  $F(\theta)$  will match the *a priori* angular distribution (2.3). In the quasi-one-dimensional regime, on the other hand, given that the clusters move with higher probability along the  $Z$  axis, we expect  $F(\theta)$  to show anomalous maxima at  $\theta=0$  and  $\theta=\pi$ .

In Fig. 10 we plot  $F(\theta)$  as computed from two systems of size  $512 \times 256$ , with very different values of  $\phi$ . The dilute system ( $\phi=0.0048$ ) is well inside the saturation regime. As we can check from this plot, its angular distribution of jumps matches quite closely the *a priori* distribution of directions, plotted as a reference in full line. In the case of the highly concentrated system ( $\phi=0.38$ ), we can observe the two peaks in  $F(\theta)$ , characteristic of the quasi-one-dimensional regime. The secondary peaks at  $\theta=\pi/2$  and  $\theta=3\pi/2$  are a spurious result of the presence, even at the large time considered, of some clusters of size  $s < s_0$  with an isotropic diffusivity. If they are removed from the statistics, the secondary peaks disappear.

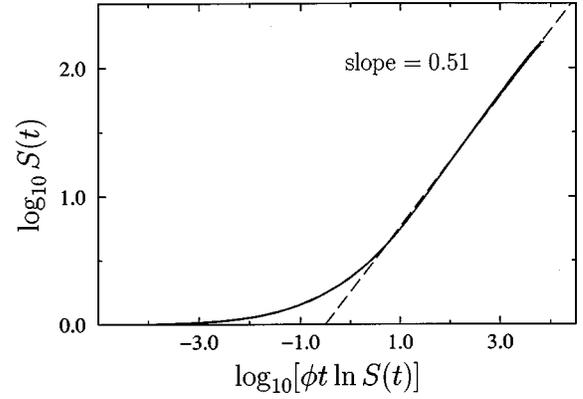


FIG. 11. Mean cluster size as a function of the rescaled quantity  $\phi t \ln S(t)$ , for anisotropic aggregation in  $d=3$ . The volume fractions plotted are  $\phi=0.0048, 0.024, 0.048$ .

#### IV. AGGREGATION IN $d=3$

Our two-dimensional model can be easily extended to  $d=3$ . In this case, the random directions of the jumps are sampled according to the distribution (2.4). Simulations have been performed for systems of size  $512 \times 64 \times 64$ . Results correspond to averages over 100 realizations.

In Fig. 11 we plot our results for the mean cluster size  $S(t)$ , for systems with an initial volume fraction  $\phi=0.0048, 0.024, 0.048$ . The average slope in the scaling region yields an exponent equal to the one obtained for two-dimensional aggregation, namely,  $\zeta=0.51$ . This fact is, however, not surprising: Since we are above the critical dimension of the problem  $d_c=2$ , we expect to find exponents independent of the dimensionality. As shown in the figure, the collapse of the mean cluster size for different volume fractions as a function of the rescaled time  $\phi t \ln S(t)$  also holds in  $d=3$ .

#### V. CONCLUSIONS

In this paper we have investigated the dynamics of the irreversible aggregation of linear rigid chains oriented along a preferred direction. A possible physical realization of such a system would be the aggregation of dipolar particles in the presence of a strong external field, oriented along the  $Z$  axis. We have proposed a Monte Carlo model, whose key ingredient is a corrected anisotropic diffusivity of the clusters, as expressed in Eq. (1.8). This diffusivity exhibits a characteristic logarithmic correction due to hydrodynamic interactions. A simple heuristic argument suggests that these logarithmic corrections should also emerge at a macroscopic scale, reflected in the asymptotic behavior of various quantities such as the mean cluster size.

We have performed extensive simulations in  $d=2$ , in a variety of system sizes and initial volume fractions. Assuming a simple power-law behavior for the mean cluster size  $S(t) \sim t^z$ , our results yield a dynamic exponent in the scaling region  $z \approx 0.61$ . This value is in excellent agreement with previous experimental works [5]. For dilute systems, the value of the dynamic exponent seems to be independent of the initial volume fraction.

Alternatively, a better fit of our data is obtained in terms of the functional relationship  $S(t)/\{\ln[S(t)]\}^\zeta \sim t^\zeta$ , which ex-

plicitly incorporates logarithmic corrections. Within this approach, the anomalous value of the dynamic exponent characterizing the aggregation of anisotropic rodlike clusters is, in fact, the consequence of the logarithmic corrections superposed to the usual power-law behavior of *isotropic* cluster-cluster aggregation.

Long-time evolutions for any value of the volume fraction  $\phi$  lead to a saturated regime, characterized by a drastic slowing down of the dynamics. The mean cluster size shows a flat region whose height and onset are exclusively functions of the system volume.

In highly concentrated systems, we observe a crossover to a quasi-one-dimensional regime. Characteristic of this transition is a sharp change in the slope of the mean cluster size, yielding a value  $\zeta = 0.32$ . To support these findings, we have carried out simulations in  $d = 1$ , where the mean cluster size exhibits a similar behavior with  $\zeta = 1/3$ . In the quasi-one-dimensional regime, clusters have a higher tendency to move along the direction parallel to their axis than in any direction perpendicular to it. This point is made clear by analyzing the jump orientation density  $F(\theta)$ .

The extension of our model to  $d = 3$  shows no significant

variations with respect to the case  $d = 2$ . This result is to be expected, given that the critical dimension of the problem appears to be  $d_c = 2$ .

To conclude, we would like to remark the potential applications of our model, especially the possibility of characterizing the aggregation of dipolar colloidal suspensions in different geometries of technological importance. For example, in a porous medium, due to the effective reduced dimensionality, we would expect a slowing down of the aggregation rate, resembling to the aforementioned quasi-one-dimensional regime.

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