

# The translational friction coefficient and time dependent cluster size distribution of three dimensional cluster-cluster aggregation<sup>a),b)</sup>

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The diffusion coefficient of clusters  $\mathcal{D}$  formed by cluster-cluster aggregation is computed according to the Kirkwood-Riseman Theory. In three dimensions one finds  $\mathcal{D}$  proportional to  $s^\gamma$  where  $s$  is the number of particles in the cluster and  $\gamma = -0.544 \pm 0.014$ . This relationship is employed to simulate the time evolution of the cluster size distribution  $N_s(t)$  which is found to exhibit simple scaling behavior  $N_s(t) \sim s^{-2}g(s/t^z)$  with  $z \sim 1.1$ .

## INTRODUCTION

Interest in nonequilibrium growth and aggregation processes has recently been stimulated by the discovery of Witten and Sander that a simple diffusion limited aggregation model leads to structures with well defined scaling and universality properties.<sup>1,2</sup> In particular, aggregates generated by the Witten-Sander model have a fractal dimensionality<sup>3</sup> which is distinctly smaller than the dimensionality of the space or lattice in which the aggregate is formed. In the Witten-Sander model, particles are added one at a time to a growing cluster or aggregate via Brownian (random walk) trajectories. As originally formulated, the Witten-Sander model generates a time ordered sequence of growth events, but time is not defined in the growth process. However, models very closely related to the original Witten-Sander model in which "time" is a well defined parameter have been developed and the rate of growth of Witten-Sander aggregates has been investigated theoretically<sup>4-6</sup> by computer simulation<sup>7,8</sup> and experimentally.<sup>9</sup>

More recently a cluster-cluster aggregation model has been developed<sup>10,11</sup> which provides a more realistic description of the aggregation processes which occur in colloidal systems. This model resembles an earlier model of Sutherland and Goodarz-Nia<sup>12</sup> in that particle-particle and cluster-cluster aggregation as well as particle-cluster aggregation processes are included. However, it differs from the Sutherland-Goodarz-Nia model because aggregation proceeds via random walk rather than linear trajectories and because time is specified in the model.

Computer simulations carried out using this model generate fractal-like structures which closely resemble those observed in metal particle aggregates.<sup>13,14</sup> In particular, the fractal dimensionality of the simulated aggregates ( $D \approx 1.8$ ) in three dimensions<sup>15</sup> is in good agreement with that found for the metal particle aggregates which are formed under conditions similar to those which the simulations are intended to represent.

We have shown, in earlier computer simulation studies,<sup>16</sup> that the structure of cluster-cluster aggregates is insen-

sitive to the way in which the cluster diffusion coefficient  $\mathcal{D}(s)$  depends on the number of particles in the cluster ( $s$ ). However, the cluster size distribution at intermediate stages during the aggregation process is sensitive to how the cluster diffusion coefficient depends on the cluster size (and other characteristics as well). The cluster diffusion coefficients are also needed to specify the time scale in the aggregation models.

The purpose of this paper is to determine the translational friction coefficient of three dimensional cluster-cluster aggregates of various sizes and shapes using the Kirkwood-Riseman theory<sup>17</sup> including hydrodynamic interactions. These results enable us to establish an approximate relationship between cluster size ( $s$ ) and the diffusion coefficient which is employed to obtain time dependent cluster size distributions<sup>18-20</sup> for cluster-cluster aggregation with translational but no rotational diffusion.

## SIMULATIONS AND CALCULATIONS

Three dimensional cluster-cluster aggregates were simulated using a three dimensional, zero concentration, off lattice model which has been described previously.<sup>21,22</sup> In this model we start out with a list of particles (single particle clusters). Pairs of clusters are randomly selected from the list, rotated to random orientations and allowed to aggregate, via a random walk without further rotation. After aggregation, the new cluster is returned to the list which is now shortened, and the process is repeated until the list consists of a single cluster containing all of the particles. Clusters containing 50-350 particles were generated in this way. Earlier work using this model<sup>21,22</sup> had led to an estimated value of about  $D \approx 1.8$  for the fractal dimensionality of aggregates.

To calculate the translational friction coefficient of these aggregates, we used the same methods which were employed to obtain the translational friction coefficient for three dimensional Witten-Sander aggregates.<sup>23</sup> The hydrodynamic interactions between the particles in the cluster were calculated using the modified Oseen<sup>24</sup> interaction ten-

tor proposed by Rotne and Prager<sup>25</sup> and Yamakawa.<sup>26</sup> The fundamental equation of this work is

$$F_i + \zeta_0 \sum_{\substack{j=1 \\ (j \neq i)}}^N T_{ij} \cdot F_j = \zeta_0 u_i, \quad i = 1, \dots, N, \quad (1)$$

where  $T$  is the hydrodynamic interaction tensor,  $F_i$  is the force exerted by the  $i$ th particle on the solvent,  $\zeta_0 = 6\pi\eta_0 a$  is the friction coefficient of each particle of radius  $a$ , and  $u_i$  is the velocity of the solvent at the  $i$ th particle;  $\eta_0$  is the solvent viscosity.

Equation (1) was solved using the numerical procedure of McCammon and Deutch.<sup>27</sup> Our results are expressed in terms of the hydrodynamic radius  $R_h$  which is given by

$$R_h = f/6\pi\eta_0, \quad (2)$$

where  $f$  is the friction coefficient. The friction coefficient  $f$  is the constant of proportionality between the total force on the cluster and the velocity with  $u_i = u$ .

A three dimensional lattice model<sup>122</sup> was used to obtain the time dependent cluster size distributions. In this model, clusters are selected at random and the selected cluster is moved in one of six equally probable directions (also selected at random) on the lattice by one lattice unit. In order to decide if the attempted move is successful or not, a random number ( $x$ ) uniformly distributed over the range  $0 < x < 1$  is generated and the move is made if  $x < \mathcal{D}/\mathcal{D}_0$ , where  $\mathcal{D}$  is the cluster diffusion coefficient and  $\mathcal{D}_0$  is the diffusion coefficient for a single particle. This procedure leads to a natural measure of time in units of *attempted* moves per cluster.

The simulations were carried out using  $(133)^3$  lattices with periodic boundary conditions. Since the time dependent cluster size distributions are sensitive to finite concentration effects,<sup>20</sup> our simulations were carried out at very low concentrations (0.0034 and 0.0021 particles per lattice site). It was necessary to average results from a number of simulations to obtain reasonably small statistical uncertainties.

## RESULTS

Clusters of seven different sizes from 50 to 350 particles per cluster at intervals of 50 particles per cluster were generated. Figure 1 shows a projection of a randomly selected cluster containing 250 particles. The radii of gyration ( $R_g$ ) and hydrodynamic radii ( $R_h$ ) were obtained for all of the clusters. By least square fitting straight lines to the coordinates  $[\ln(R_g), \ln(s)]$  a radius of gyration exponent ( $\beta$ ) of  $0.554 \pm 0.038$  was obtained assuming that  $R_g \sim s^\beta$ . This value of  $\beta$  corresponds to an effective fractal dimensionality ( $D_\beta$ ) of  $1.81 \pm 0.13$  in good agreement with our earlier results obtained from much larger scale simulations.

The dependence of the hydrodynamic radius on cluster size can also be fitted to a power law relationship of the form  $R_h \sim s^{-\gamma}$ , where the exponent  $-\gamma$  has a value of  $0.544 \pm 0.014$ . Figure 2 shows the dependence of  $\ln(R_h)$  on  $\ln(s)$  for the 133 clusters used in this work.

At the outset of this work we anticipated that the statistical uncertainties in the exponent  $\gamma$  would be quite large and that it might be better to seek a relationship between  $R_h$  and  $R_g$  of the form  $R_h \sim R_g^\delta$ . However, a linear regression analysis leads to the result  $\delta = 0.895 \pm 0.395$ . The uncertainties

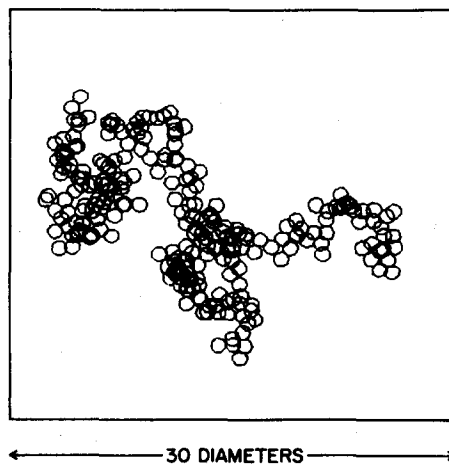


FIG. 1. A projection on a plane of a typical three dimensional cluster of 250 particles generated using the off lattice, zero concentration cluster-cluster aggregation model. The figure illustrates the very open structure of these aggregates.

given for the exponents  $\beta$ ,  $\gamma$ , and  $\delta$  are two times the standard error. Consequently, we conclude that  $R_h$  is much more strongly correlated with  $s$  than with  $R_g$ . The uncertainties in the numerical results do not allow us to attribute any significance to the observation that  $R_h$  increases with the number of particles in a cluster  $s$  more slowly than  $R_g$  [ $(-\gamma) < \beta$ ]. It is likely that the difference in the apparent exponents for these two quantities is attributable to the slow approach of  $R_h$  (compared to  $R_g$ ) to the asymptotic regime  $s \rightarrow \infty$ . In the asymptotic regime we expect  $(-\gamma) = \beta$ . The reasons for the difference in the approach of  $R_h$  and  $R_g$  to asymptotic regime for cluster-cluster or diffusion limited aggregates is likely to be similar to the reason given by Weill and Des Cloizeaux<sup>28</sup> for the same behavior seen with linear polymer.

To calculate the hydrodynamic radius for a cluster of 350 particles requires about 30 min of computer time on an IBM 3081 computer. Clearly it is not practical to calculate the hydrodynamic radius for all of the clusters formed in a simulation of cluster-cluster aggregation. Consequently, we use the result  $R_h \sim s^{-\gamma}$  or  $\mathcal{D}(s) \sim s^\gamma$  ( $\simeq -0.545$ ) for the simulation of the estimated time evolution of cluster size distributions.

Lattice model simulations of cluster-cluster aggregation were carried out using 5000 and 8000 particles or occupied lattice sites on  $(133)^3$  lattices with periodic boundary conditions. Figure 3(a) shows the time dependent cluster size distribution obtained from the simulations carried out using

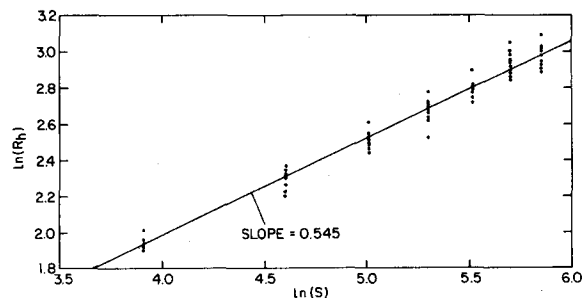


FIG. 2. The dependence of hydrodynamic radius ( $R_h$ ) on cluster size ( $s$ ) for 133 clusters in the size range  $50 < s < 350$  particles.

8000 particles on  $(133)^3$  lattices ( $p = 0.0021$  particles per lattice site). The results from 60 simulations were averaged to obtain the results shown in Fig. 3(a). It has recently been shown<sup>18-20</sup> that the time dependent cluster size distribution exhibits simple scaling behavior of the form

$$N_s(t) \sim s^{-2} g(s/t^z), \quad (3)$$

where  $g$  is a scaling function which depends on the diffusion exponent  $\gamma$ .

The quantity  $s^{-2}$  on the right-hand side of Eq. (3) and the common tangent with a slope of  $-2$  in Fig. 3(a) are a direct consequence of mass conservation in the simulations.<sup>18-20</sup> To better illustrate the scaling behavior for  $N_s(t)$ , the results shown in Fig. 3(a) are replotted in Fig. 3(b). From Fig. 3(b), it is clear that the scaling relationship given in Eq. (3) is obeyed at long times and that the scaling exponent  $z$  has a value of about 1.1. Similar results were obtained from the simulations carried out at a higher density (0.0034 particles per lattice site).

## DISCUSSION

We have calculated the translational friction coefficients for three dimensional aggregates formed by diffusion limited cluster-cluster aggregation and employed the results of these calculations to obtain a relationship between cluster diffusivity and cluster size [ $\mathcal{D}(s) \sim s^\gamma$ ;  $\gamma = -0.544 \pm 0.014$ ]. This relationship has been used to obtain the time dependent cluster size distribution,  $N_s(t)$  from lattice model simulations of cluster-cluster aggregation. Because the lat-

tice models do not allow cluster to rotate, our procedure is self-consistent.

In real colloidal systems, rotational diffusion may play an important role. Recent results of computer simulations and theory have shown that rotational diffusion can have important effects on the structure of aggregates formed by cluster-cluster aggregation.<sup>29,30</sup> Our treatment also ignores hydrodynamic interactions between the aggregating clusters and the effects of attractive and repulsive interactions.

Despite these deficiencies, the results presented in this paper are a step towards obtaining a better understanding of coagulation when diffusional encounters are rate limiting.

The value obtained for the diffusion coefficient exponent ( $\gamma$ ) is quite close to the critical value ( $\gamma_c$ ) of about  $-0.5$  found recently for three dimensional cluster-cluster aggregation.<sup>20</sup> For values of  $\gamma$  larger than  $\gamma_c$ , the cluster size distribution function  $N_s(t)$  decreases monotonically with increasing cluster size. For  $\gamma < \gamma_c$ , there is a maximum in the cluster size distribution. In our case,  $\gamma$  is slightly smaller than  $\gamma_c$  and a broad maximum is found.

Our results can be understood in terms of the mean field, Smoluchowski equation<sup>31</sup> in which the time evolution of the concentration of clusters containing  $k$  particles ( $C_k$ ) is given by

$$dC_k/dt = 1/2 \sum_{i+j=k} K_{ij} C_i C_j - C_k \sum_{j=1}^{\infty} K_{kj} C_j. \quad (4)$$

In this equation  $K_{ij}$  is the rate constant for addition of monomers of size  $i$  to monomers of size  $j$ . Since the structures formed by cluster-cluster aggregation cannot interpenetrate each other the reaction constant  $K_{ij}$  (in three dimensions) will be given by<sup>32</sup>

$$K_{ij} \sim (R_i + R_j)(\mathcal{D}_i + \mathcal{D}_j). \quad (5)$$

Here  $R_i$  is an appropriately averaged radius for clusters containing  $i$  particles.

In the asymptotic (large cluster size) limit Eq. (5) becomes

$$K_{ij} \sim (i^{1/D} + j^{1/D})(i^{-\gamma} + j^{-\gamma}). \quad (6)$$

For the case  $\gamma = 1/D$  we have

$$K_{ij} \sim (i^{1/D} + j^{1/D})(i^{-1/D} + j^{-1/D}). \quad (7)$$

Recent computer simulations<sup>33</sup> have shown that Eq. (6) is at least a good approximation for cluster-cluster aggregation in three dimensions (even for quite small clusters).

Exactly analytical solutions of the Smoluchowski equations do not exist for reaction kernels of the form given in Eqs. (6) and (7). However, the rate constants ( $K_{ij}$ ) depend only weakly on the cluster sizes  $i$  and  $j$ . In particular the kinetic kernel  $K$  has the symmetry property  $K_{(\lambda i)(\lambda j)} = K_{ij}$ . For this reason we are prepared to assume that the time dependent cluster size distribution will exhibit the same asymptotic scaling properties as that found for the Smoluchowski equation with size independent rate constants. In this case the cluster size distribution is given by<sup>31</sup>

$$N_s(t) = t^{s-1} / (1+t)^{s+1} \quad (8)$$

which can be described by either of the two scaling forms

$$N_s(t) \sim t^{-2} g(s/t) \quad (9a)$$

or

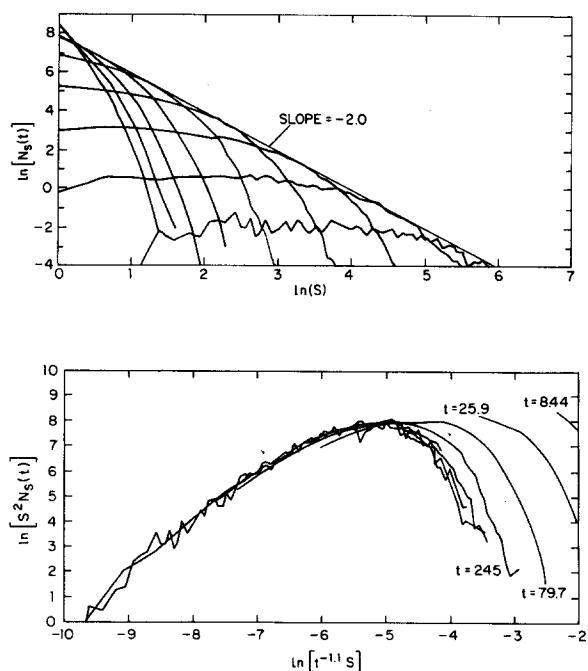


FIG. 3. (a) This figure shows the time dependent cluster size distributions obtained from the three dimensional lattice model simulations carried out using 5000 particles on  $(133)^3$  lattices.  $N_s(t)$  is the average number of cluster containing  $s$  particles at time  $t$ . The units is in units of average number of attempted moves per cluster. The curves were determined at the times 2.75, 8.44, 25.9, 79.7, 245, 752, 2311, 7100, and 21 800 attempted moves per cluster. (b) In this figure, the application of the scaling relationship given in (a) is demonstrated. At long times, the results fall on a common curve. The cluster size distribution does not scale at short times.

$$N_s(t) \sim s^{-2} f(s/t), \quad (9b)$$

indicating that the scaling exponent  $z$  has a value of 1.0. The result  $z \simeq 1.1$  is in quite good agreement with the expectation that  $z$  should have a value of 1.0. The fact that the value we obtain for  $z$  is slightly larger than 1.0 may be a result of the finite size and finite concentration of our simulations which prevent us from approaching the long time limit in which Eq. (9b) is expected to be valid.

The values obtained for the exponents describing how the radius of gyration and hydrodynamic radius grow with increasing cluster size are equal within the accuracy of our simulation results. However, the value used for  $-\gamma$  (0.545) in our simulations of the time dependent cluster size distributions is slightly smaller than our best estimate for the radius of the gyration exponent from lattice model simulations of cluster-cluster aggregation<sup>22</sup> ( $\beta \simeq 0.57$ ). This will slightly increase the value of  $z$ . According to the recent theoretical work of Botet and Jullien,<sup>34</sup> the exponent  $z$  is given by

$$z = 1/(1 - \gamma - \beta) \quad (10)$$

or

$$z = 1.03 \quad \text{for } \gamma = -0.545 \text{ and } \beta = 0.57.$$

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