Translational friction coefficient of diffusion limited aggregates

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electron spin resonance, laser-induced photochemistry and fluorescence, etc. Our studies have shown that the extent of orientational ordering is largely controlled by deposition conditions (temperature, rate, and pulsed vs slow spray-on) and that the effect can be quantified by polarization studies.

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Translational friction coefficient of diffusion limited aggregates[a]

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Recently there has been considerable interest in the diffusion controlled growth of particle clusters.[1–8] Computer simulations reveal[1,2] that the structure of these aggregates is highly ramified with a shape characterized in terms of the radius of gyration R and the number of particles aggregated, N, according to

$$N = \rho R^{D}, \tag{1}$$

where ρ is a dimensional constant and $D = \eta d$ with η equal to approximately (5/6) for spatial dimension $d = 2,3,4$. The highly open structure of the aggregates, in contrast to classical spherical clusters where $\eta = 1$, $D = d$, suggests that the frictional properties of these clusters may differ considerably from the conventional results for compact structures. The frictional properties of these particles therefore deserve attention.

The purpose of this note is to report results for the translational friction coefficient $f(N)$ for clusters of various sizes and shapes in $d = 3$, calculated according to the Kirkwood–Riseman theory[9] in the presence of hydrodynamic interaction between the N particles which compose the cluster.

The fundamental equation of this work is

$$\mathbf{F}_i + \zeta_0 \sum_{\substack{j=1 \\ (j\neq i)}}^{N} \mathbf{T}_{ij}\cdot\mathbf{F}_j = \zeta_0 \mathbf{U}_i, \quad i = 1,...,N, \tag{2}$$

where $\mathbf{F}_i$ is the force exerted by the ith particle on the solvent, $\zeta_0 = 6\pi\eta_0 a$ is the friction coefficient of each particle of radius a, and $\mathbf{U}_i$ is the velocity of the solvent at the ith particle; η_0 is the solvent viscosity.

In Eq. (2) $\mathbf{T}_{ij}$ is the hydrodynamic interaction tensor. Because an anomalous result sometimes arises when the Oseen tensor is employed,[11] we use the modified version of Oseen tensor as suggested by Rotne and Prager[12] and Yamakawa[13] for the hydrodynamic interaction tensor,

$$\mathbf{T}_{ij} = (8\pi\eta_0 r_{ij})^{-1} \left\{ [\mathbf{I} + (\mathbf{r}_{ij}\mathbf{r}_{ij}/r_{ij}^2)] + \left(\frac{2a^2}{r_{ij}^2}\right)[\tfrac{1}{3}\mathbf{I} - (\mathbf{r}_{ij}\mathbf{r}_{ij}/r_{ij}^2)] \right\},$$

where $\mathbf{r}_{ij}$ is the difference in position between particles i and j.

The matrix Eq. (2) has been solved for 14 different cluster configurations for various number of particles employing a numerical method described by McCammon and Deutch.[10] The clusters are not permitted to rotate and the total force $\mathbf{F}_T = \Sigma_i \mathbf{F}_i$ is determined in response to a uniform velocity $\mathbf{U}_i = \mathbf{v}$ in a specific direction $\alpha = x,y,z$. The friction coefficient is obtained from the relation $f_T^{\alpha} = f_{\alpha}(N)\mathbf{v}_{\alpha}$ and the average friction coefficient is determined according to $F(N)^{-1} = \frac{1}{3}[\Sigma_{\alpha} F_{\alpha}^{-1}(N)]$.

In the nonfree draining limit where the hydrodynamic interaction will exclude solvent from the cluster interior one expects $f = 6\pi\eta_0 R'$, where R' is the cluster hydrodynamic radius. If R' is assumed to be proportional to the radius of gyration $R(N)$ as given by Eq. (1) one is led to

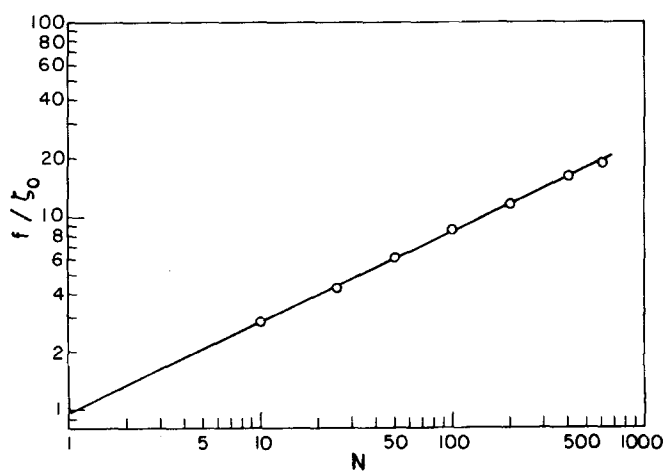

FIG. 1. Average translation friction coefficient vs number of particles in cluster N in log–log plot. ζ_0 is friction coefficient of single particle.

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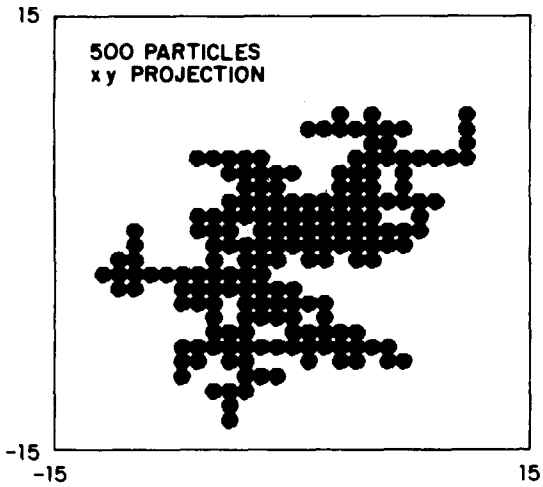

FIG. 2. Illustrative projection of 500 particle cluster; (30×30) portion of the $d = 3$ lattice on which the simulation was made.

$$\ln[f(N)/\zeta_0] = \ln c + \beta \ln N. \tag{3}$$

For Eq. (1), the predicted coefficient is $\beta = (1/D) = (1/\eta d) = (6/5d)$ [$\beta = 2/5$ for $d = 3$] and $c = [a\rho^{1/D}]^{-1}$. In contrast, the prediction in the case of free draining, $F = \zeta_0 N$, is $\beta = 1$ and in the case of classical compact aggregates, the prediction is $\beta = 1/d = 1/3$ for $d = 3$.

Our results for a typical cluster, arbitrarily designated No. 3DCD2, for values of N from 1 to 600 are plotted in Fig. 1 as $\ln[F(N)/\zeta_0]$ vs $\ln N$. A plane projection of a typical cluster configuration is presented in Fig. 2.

The result for the best fit for the cluster (No. 3DCD2) extending to $N = 600$, excluding $N = 1$, *is*

$$\beta = 0.47. \tag{4}$$

The precise value for this coefficient depends upon the manner in which the data are handled but all reasonable procedures lead to values in the range $0.46 < \beta < 0.48$.

For example the best fit for 61 data points from 14 clusters with N up to 600, but excluding $N = 1$, is $\beta = 0.479$ while $\beta = 0.460$ based on two points [$N = 1$ and $N = 600$] for cluster No. 3DCD2. If the fit to the data points is constrained to pass through the exact result $f(1) = \zeta_0$ the β is found to be $\beta = 0.469$.

The surprising feature of the calculations is the relatively modest dispersion in the results for f at even small cluster sizes. For example, the standard deviation of the data for 14 clusters of a $N = 10$ is 8.8% of the average $f(10)$. However when the cluster size has grown to $N = 200$, the standard deviation has fallen to 2.3% of the average $f(200)$ for ten different clusters. The data for finite N extrapolate to a value for a single particle slightly below the exact result $f(1) = \zeta_0$.

The value of $\beta = 0.47 \pm 0.01$ is somewhat greater than the prediction $\beta = 0.40$ based on an equivalent average sphere. This difference is not surprising since the microscopic cluster structure includes particles located at significant distances from an average R. The data do not support the use of the classical value of $\beta = 1/3$ for these aggregates.

These results provide a basis for assigning a friction coefficient and hence diffusion coefficient to clusters of various sizes which may be employed to model aggregation in these diffusion limited systems when both the clusters and individual particles are mobile.[14]

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