Comment on "Hydrodynamic Behavior of Fractal Aggregates"

A recent Letter[1] by Wiltzius was concerned with an important dynamic parameter—the hydrodynamic radius (R_H)—and its relationship with the radius of gyration (R_G). Using static and dynamic light scattering, he studied the slow aggregation of colloidal silica particles and found that the ratio R_H/R_G for aggregates in the size range 500 Å $\leq R_H \leq$ 7000 Å had a constant value of 0.72 ± 0.02. These aggregates have a fractal dimensionality (D) of about 2.1. Wiltzius referred to our calculations of the ratio R_H/R_G for three-dimensional diffusion-limited cluster-cluster aggregates ($D \simeq 1.78$) and pointed out a serious disagreement between his measurements and our predictions. Our initial investigation[2,3] of the hydrodynamic behavior was concerned with the scaling of the hydrodynamic radius with the aggregate mass. Consequently, we did not carefully look at the numerical value of the ratio R_H/R_G. The value of 1.75 was given in private correspondence with a caution that we had not been very much concerned with R_H/R_G and that our result might be off by a factor of 2 or π.

Recently, we reexamined our calculation and found that our value for R_H/R_G should be reduced by a factor of 2. The hydrodynamic radius for diffusion-limited cluster-cluster aggregates which we published in Ref. 3 was given in units of the monomer radius, while the radius of gyration (which we did not publish) was expressed in terms of the bond length. Since the bond length is twice the monomer radius, our value for R_H/R_G should be reduced by a factor of 2. Our results for 133 clusters in the size range of 50–350 particles indicate that R_H/R_G has a value of about 0.875 independent of the cluster size.

Our calculation is based on solution of the hydrodynamic interaction between each pair of particles in the cluster self-consistently, and the total force and the hydrodynamic radius can then be obtained. The fundamental equation is

$$\mathbf{F}_i + \zeta_0 \sum_{\substack{i,j \\ i \neq j}} \mathbf{T}_{ij} \cdot \mathbf{F}_j = \zeta_0 \mathbf{U}_i, \quad i = 1, \ldots, N,$$

where $\mathbf{F}_i$ is the force exerted by the ith particle on the solvent, $\zeta_0 = 6\pi\eta a$ is the friction coefficient of each particle of radius a, and $\mathbf{U}_i$ is the unperturbed velocity of the solvent at the ith particle; η is the solvent viscosity. $\mathbf{T}_{ij}$ is the hydrodynamic interaction tensor. In our calculation a modified Oseen tensor suggested by Rotne and Prager[4] and Yamakawa[5] was used. This scheme does not involve a preaverage approximation as used in Ref. 1 [Eq. (6)] and thus gives more accurate description for hydrodynamic interaction. For chains formed by a random-walk model our preliminary calculation[6] gives $R_H/R_G = 0.87$ for 14 clusters in the size range of 300–600 particles, while the measurement of similar but flexible chains—polystyrene chains in θ solvents—gives $R_H/R_G = 0.79 \pm 0.04$.[7] For highly ramified irregularly shaped objects such as fractal clusters the numerical solution for the above equation should provide insight into the hydrodynamic behavior of fractal objects.

We have recently calculated the value of R_H/R_G for aggregates obtained from an off-lattice model[8] for reaction-limited aggregation.[9] This model generates clusters with a fractal dimension of about 2.1 which should more closely resemble the silica-particle aggregates studied by Wiltzius than do the diffusion-limited aggregates used in our earlier work. The results obtained from these calculations are given in the following table.

Size of cluster	50	100	200	400
R_H/R_G	0.96	0.965	0.95	0.985
Number of clusters averaged	15070	2720	250	205

Again, we find that R_H/R_G is almost independent of the cluster size and has a value of about 0.97. This is still somewhat larger than the result of 0.72 ± 0.02 found by Wiltzius, but in view of the uncertainties associated with both the experiments and the simulations and the fact that the reaction-limited aggregation model may not completely describe the structure of the silica-particle aggregates, we believe that the experimental and calculated values for R_H/R_G are in substantial agreement.

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