Hydrodynamic Behavior of Fractal Aggregates

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Measurements of the radius of gyration R_G and the hydrodynamic radius R_H of colloidal silica aggregates are reported. These aggregates have fractal geometry and R_H is proportional to R_G for 500 Å $\leq r_H \leq$ 7000 Å, with a ratio $R_H/R_G = 0.72 \pm 0.02$. The results are compared with predictions for macromolecules of various shapes. The proportionality of the two radii can be understood with use of the pair correlation function of fractal objects and hydrodynamic interactions on the Oseen level. The value of the ratio remains to be explained.

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The concept of fractal geometry has proven successful for the description of nonequilibrium aggregation in colloidal and macromolecular systems. A variety of techniques such as light, x-ray, and neutron scattering[1-3] and electron microscopy,[4] as well as computer simulations,[5-7] have been used to probe the signature of fractal structures obtained for various growth mechanisms relating their masses to their radii via $M \propto R^{d_f}$, where the fractal or Hausdorff dimension d_f differs from the dimensionality of the Euclidean space. For slow aggregation of silica[1,8] or gold[3] colloids it is well established that $d_f = 2.08 \pm 0.05$ and recent numerical simulations of the cluster aggregation model[6,7] in the limit of very small sticking probability[9] are in agreement with the *in situ* measurements.[1] So far most of the effort has been concentrated on the purely geometric aspects of aggregates produced by various growth processes.

It is the purpose of this Letter to address the Brownian dynamics behavior of fractal structures and the relationship between the hydrodynamic and static properties. To this end I studied slowly aggregating colloidal silica spheres *in vitro* with static and dynamic light scattering. I find that the hydrodynamic radii R_H obtained from the translational diffusion coefficient of the aggregates are proportional to their radii of gyration R_G in the range 500 Å $\leq R_H \leq$ 7000 Å with a ratio $R_H/R_G = 0.72 \pm 0.02$. The proportionality of the two radii can be explained with use of Kirkwood's approximation[10,11] for diffusion of complex, rigid macromolecules. The value of the ratio, however, is strongly at variance with $R_H/R_G = 1.75$ obtained[12] for simulated cluster-cluster aggregates. The latter calculations seem to overestimate greatly the hydrodynamic friction of fractal objects. We observe, however, intriguingly close agreement with the experimental values measured for linear random-walk polymer chains in solution[13] ($R_H/R_G = 0.79 \pm 0.04$). It is interesting to note that both the silica clusters and linear random-walk polymers have very similar Hausdorff dimensions, $d_f = 2.08$ and $d_f = 2$, respectively, yielding similar mass distributions within the aggregates. The internal motions, which are big in flexible polymer chains and small in the rigid, slowly grown silica aggregates,[8] have only minor influence on the diffusive behavior of these macromolecules.

The relationship between the mass of a cluster and its diffusion coefficient D plays a crucial role[14] in simulations of aggregation processes. Typically D is assumed to be proportional to M^{γ} and the value of the parameter γ has a profound influence on the cluster size distribution. The present results establish that D is proportional to M^{-1/d_f}, and also justify the *a priori* assumption[3,15] that R_H is proportional to a static radius.

The samples were prepared by diluting of commercially available silica spheres (LUDOX SM, Dupont, diameter 70 Å) to a concentration of 0.08% by weight. The salinity of the solution was 0.5*M* NaCl. Under these conditions aggregation was very slow and it took clusters 7 days to grow to a size ≥ 1 μm. Static and quasielastic light-scattering experiments were performed with an apparatus similar to the one described by Haller, Destor, and Cannell.[16] The light source was a 7-mW He-Ne laser and the scattering light was collected at fifteen different angles corresponding to scattering wave vectors 2.6×10^4 cm$^{-1} \leq q \leq 2.6 \times 10^5$ cm^{-1}. The temperature of the sample was stabilized at 25 ± 0.1 °C.

The results from static light-scattering experiments are presented in Fig. 1. The weight-averaged molecular weight (in arbitrary units) and the average radius of gyration were obtained from the angular dependence of the scattered light intensity. For the data analysis I used a Fisher-Burford-type approximant[17]

$$S(q) \propto M_w [1 + 2q^2 R_G^2 / 3d_f]^{-d_f/2}, \tag{1}$$

which has the correct asymptotic behavior for scattering objects with fractal geometry. For 600 Å $\leq R_G \leq$ 8000 Å the data exhibit power-law behavior of the form

$$M_w \propto R_G^{2.10 \pm 0.03}. \tag{2}$$

This is characteristic for self-similar, fractal aggregates and the observed Hausdorff dimension $d_f = 2.10 \pm 0.03$ is in excellent agreement with results obtained under

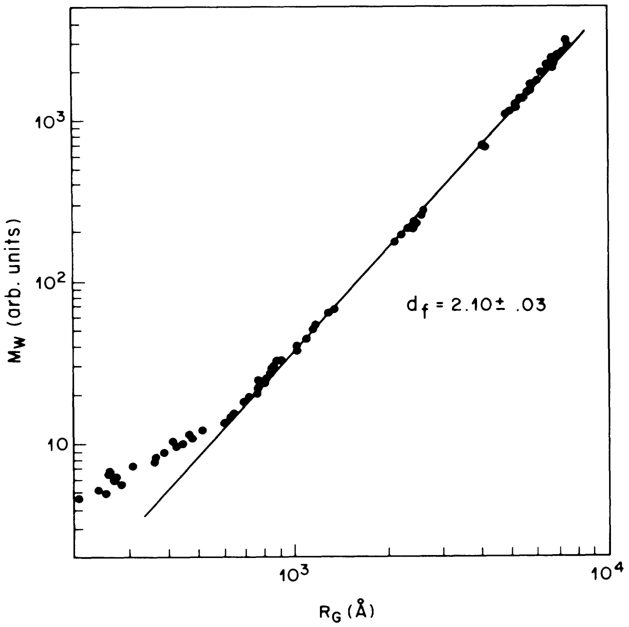

FIG. 1. The average molecular weight as a function of radius of gyration for aggregating colloidal silica spheres (monomer radius 35 Å). The power-law behavior indicates fractal geometry of the clusters with a Hausdorff dimension $d_f=2.10\pm0.03$.

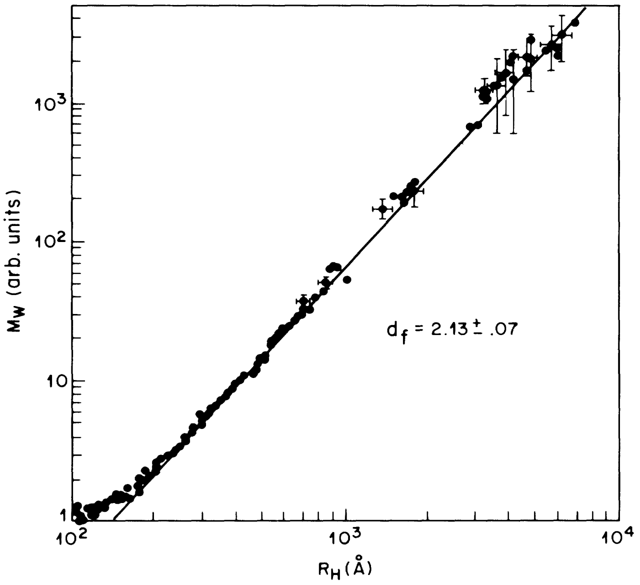

FIG. 2. The average molecular weight as a function of hydrodynamic radius of the aggregates of Fig. 1. The hydrodynamic radius was obtained from the diffusion coefficient.

similar conditions in previous experiments.[17,18]

The average hydrodynamic radius of the aggregates was obtained from quasielastic light-scattering experiments. The initial decay rate Γ of the fluctuations in the scattered light intensity was determined from a cumulant analysis of the measured autocorrelation function. The decay rate depends on the length of the wave vector q and it can be shown[19] that Γ/q^2 becomes q independent in the limit of small q and approaches the translational diffusion coefficient D. D in turn can be related to a hydrodynamic radius R_H via an Einstein-Stokes relation $D=k_B T/6\pi\eta_0 R_H$, where k_B is Boltzmann's constant, T the temperature, and η_0 the solvent viscosity. At various stages of aggregation I measured Γ as a function of q and extrapolated Γ/q^2 to $q=0$. I found empirically that the best description of the q dependence of the data is given by the following *ad hoc* series expansion:

$$\Gamma=(k_B T/6\pi\eta_0 R_H)q^2(1+0.165qR_H). \tag{3}$$

The values thus obtained for R_H are plotted in Fig. 2. As in Fig. 1, I observe power-law behavior

$$M_w \propto R_H^{2.13\pm0.07} \tag{4}$$

for 250 Å $\leq R_H \leq$ 7000 Å. We want to note that the three quantities M_w, R_G, and R_H grow exponentially with time. The aggregates reach a size of $R_H=7000$ Å beyond which they sediment. The maximum obtained value of $qR_H=18.3$ shows that the linear term in the above series expansion does not become dominant under the present conditions. Thus we do not enter the high-q regime where $\Gamma\propto q^{2.7}$ was observed[20] for fractal aggregates.

Figure 3 is a plot of R_H as a function of R_G at various stages of the aggregation. In the range 500 Å $\leq R_H \leq$ 7000 Å I find that to within experimental accuracy the hydrodynamic radius is proportional to the radius of gyration and the ratio is $R_H/R_G=0.72\pm0.02$. For 200 Å $\leq R_H \leq$ 600 Å this ratio is systematically bigger, which is not surprising since the size of the aggregates is still comparable to the monomer diameter and the concept of self-similarity is not meaningful.

Fractal objects with $d_f \geq 2$ are opaque in three dimensions and in a simple attempt to understand the data we might treat the silica aggregates as dense. The translational friction coefficient for prolate ellipsoids of revolution with an axis ratio $\rho \leq 1$ has been calculated by Perrin[21] and can be formulated as

$$\frac{R_H}{R_G}=\left[5\frac{1-\rho^2}{1+2\rho^2}\right]^{1/2}\left[\ln\left[\frac{1+(1-\rho^2)^{1/2}}{\rho}\right]\right]^{-1}. \tag{5}$$

For spheres ($\rho=1$), Eq. (5) yields $R_H/R_G \approx 1.29$, which is an upper limit for the ratio. Large-scale computer simulations of the cluster-cluster aggregation model have shown that the aggregates become asymmetric with aspect ratios of about 2. For $\rho=\frac{1}{2}$ Eq. (5) yields $R_H/R_G \approx 1.20$, which is also too large. In order to find better agreement with the data we would have to make

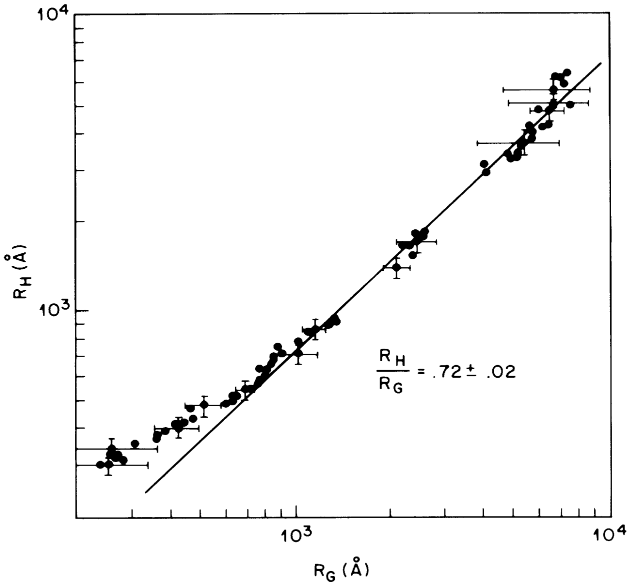

FIG. 3. The hydrodynamic radius as a function of the radius of gyration of aggregates with fractal geometry. The line has a slope of 1.

the unlikely assumption that the aggregates are almost rodlike with $\rho = 0.1$ in which case $R_H/R_G \approx 0.74$.

Since this simple approach is unsatisfactory I am going to adopt Kirkwood's approximation[10,11] for hydrodynamic properties of complex, rigid macromolecules. These structures are composed of N identical spherical units rigidly linked together. If the flow-velocity field were unperturbed within the aggregate, every unit would experience the same friction proportional to its radius. The total viscous force would thus be proportional to N and R_H proportional to $R_G^{d_f}$ in strong disagreement with my results. This means that hydrodynamic screening is high which is taken into account in Kirkwood's approximation for the translational diffusion coefficient,

$$D = (k_B T/6\pi\eta_0)\textstyle\sum_{ij} R_{ij}^{-1}/N^2, \tag{6}$$

where the summation is over all units i and j separated by a distance R_{ij} within a given macromolecule. The sum in (6) basically reflects Oseen's approximation that hydrodynamic interactions decay like $1/r$. Replacing the summation by an integration and using the pair correlation function we find

$$D = (k_B T/6\pi\eta_0)\int_0^\infty dr\, r g(r)\left[\int_0^\infty dr\, r^2 g(r)\right]^{-1}, \tag{7}$$

expressing a hydrodynamic quantity in terms of static properties. Equation (7) together with the definition of the radius of gyration finally yields

$$\frac{R_H}{R_G} = \frac{\int_0^\infty dr\, r^2 g(r)}{\int_0^\infty dr\, r g(r)}\left\{\frac{2\int_0^\infty dr\, r^2 g(r)}{\int_0^\infty dr\, r^4 g(r)}\right\}^{1/2}. \tag{8}$$

For fractal aggregates the pair correlation function can be written as

$$g(r) \propto r^{d_f - 3} f(r/R_c), \tag{9}$$

where $f(r/R_c)$ is a cutoff function decaying strongly enough to make the integrals in (8) converge. Combination of (8) and (9) leads to the prediction

$$R_H \propto R_G, \tag{10}$$

independent of d_f and R_c. The value of the ratio depends on the cutoff function. A step function yields $R_H/R_G = 1.03$, whereas an exponential cutoff gives $R_H/R_G = 0.62$, showing the importance of a correct treatment of the interactions at the perimeter of the aggregates.[22]

To my knowledge there is only one prediction for the ratio R_H/R_G based on numerical evaluation[12] of the friction coefficient of aggregates simulated for the cluster-cluster aggregation model.[6,7] The value 1.75 disagrees strongly with my experimental result $R_H/R_G = 0.72 \pm 0.02$.

The determination of the ratio has spurred extensive theoretical and experimental activity in the case of linear polymers[13] in solution. For linear, flexible, random-walk chains a wealth of data shows that $R_H/R_G = 0.79 \pm 0.04$ independent of the chemical details of the polymers or the solvents. Interestingly, the fractal dimension $d_f = 2$ of these chains is similar to the one measured for silica aggregates indicating an intimate relationship between the ratio R_H/R_G and the Hausdorff dimension. It is surprising that the flexibility of the polymers or the stiffness[8] of the silica aggregates does not play an important role in the diffusive behavior. Further theoretical work to elucidate these experimental facts is highly desirable.

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