Physica 147A (1987) 280–296
North-Holland, Amsterdam

ON THE HYDRODYNAMIC RADIUS OF FRACTAL AGGREGATES

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Motivated by recent light scattering experiments by Wiltzius, we discuss the various factors affecting the hydrodynamic radius R_H of fractal aggregates, underlining the need for further experiments. After a critical discussion of the results of the Kirkwood–Riseman approximation for the hydrodynamic radius, we analyze the porous sphere model of Debye–Bueche and Brinkman. For spherically symmetric aggregates this model leads to values of R_H which are substantially larger than found experimentally by Wiltzius, but somewhat smaller than found in numerical simulations. We make various suggestions for the physical origin of these discripancies, and argue that they might be due to asymmetry of the aggregates. We discuss how this suggestion can be tested experimentally with depolarized light scattering as well as with sedimentation experiments, and theoretically with the aid of computer simulations.

1. Introduction

In view of Peter Mazur's life-long interest in Brownian motion[1–5]) and the statistical properties of particles in suspension[6]), it seems appropriate at this occasion to discuss a problem of this type. I will therefore discuss some aspects of a topic of current interest, the hydrodynamic radius of fractal aggregates, using some results related to an approach popularized in the seventies by Mazur and Bedeaux[7,8]) in their extension of the so-called Faxén theorems[9]) for the hydrodynamic friction and torque on particles in suspension.

The present work was motivated directly by recent experiments by Wiltzius[10]). In his experiments on slowly aggregating silica spheres, Wiltzius[10]) used static and dynamic light scattering to determine simultaneously the radius of gyration R_G and the hydrodynamic radius R_H (defined through the translational diffusion coefficient) of the aggregates. The aggregate formation in his experiments is reaction limited; indeed the observed fractal dimension $d_f \simeq 2.10 \pm 0.03$ of the aggregates is close to the fractal dimension obtained in simulations of the reaction limited aggregation model in three dimensions[11,12]).

For large cluster sizes, Wiltzius[10]) found the ratio R_H/R_G (which we will refer to as the *hydrodynamic ratio*) to approach a constant value of about 0.72 ± 0.02. This experiment is therefore the first to show explicitly that the hydrodynamic radius of large fractal aggregates is indeed proportional to the radius of gyration of the aggregate, as had been suggested by Chen et al.[13,14]) on the basis of numerical simulations. This proportionality is an important ingredient for describing the aggregation kinetics, since the coagulation kernel of the Smoluchowski equation that models this kinetics is usually assumed to be proportional to the radius of gyration of the particles and their diffusion coefficient. The proportionality of R_H and R_G then implies that the coagulation kernel has only a weak dependence on the particle size[14–16]). (Different behavior can be found, e.g. under flame conditions[16]), when the mean free path of the gas molecules is of the order of the size of the particles[16,17]).)

Of course, the fact that the hydrodynamic radius of large fractal aggregates becomes proportional to their radius of gyration, is intuitively not at all surprising. For, the formation of fractal structures is intimately connected with the screening of the diffusion field from the interior of the aggregate[18]). As a result, the growth takes place only at an outer "active growth zone"[18,19]) whose width scales with the size of the aggregate[20]). If we disregard the complications due to its vector character, the hydrodynamic velocity field obeys an equation much like the Laplace equation for the probability distribution governing the growth of the aggrregate. Therefore, one likewise expects the hydrodynamic field to be screened from the interior of the aggregate for all $d_f > 1$ [18]) and so $R_H \propto R_G$. Moreover, as discussed by Wiltzius[10]) and Hess et al.[21]), the proportionality of R_H and R_G also emerges quite naturally in the Kirkwood–Riseman[22,23]) approximation, a fact which is actually well-known in the polymer literature[24]).

What then is the reason for undertaking the present study? Our motivation is two-fold. First of all, while the proportionality of R_H and R_G may be no surprise, we will argue that the value of the hydrodynamic ratio found by Wiltzius[10]) is smaller than can reasonably be expected for spherically symmetric aggregates, and that the experiments therefore indicate that there is some interesting physics to be understood. In particular, Wiltzius[10]) mentions unpublished work by Meakin[25]) in which he found a hydrodynamic ratio of about 1.75 in simulations of a different cluster–cluster aggregation model than the one relevant for the experiments of Wiltzius[10]), about a factor of $2\frac{1}{2}$ larger than the experimental values. (*See note added in proof.*) On the other hand, the two theoretical estimates of the Kirkwood–Riseman[22,23]) theory (1.02 with a sharp cutoff and 0.62 with an exponential cutoff) seem to bracket the experimental value of 0.72 nicely. We will present arguments, however, why it is likely that the latter estimates are too small for spherically symmetric clusters, and then show that an approach based on the porous sphere model of Debye and Bueche[26,27]) and of Brinkman[28]) yields indeed substantially larger values for the hydrodynamic ratio. For large spherically symmetric aggregates with a fractal dimension of 2.07, as in the experiments, the model predicts a hydrodynamic ratio of about 1.23, about a factor of 1.7 larger than the experimental value and somewhat less than Meakin's value[25]) quoted above. Although we have no definite explanation for the discrepancy between ours as well as Meakin's estimate on the one hand and the experimental value on the other hand, we will tentatively suggest that this may be due to the anisotropy of the aggregates, and discuss how this can be checked.

A second motivation for this work is the fact that in the treatments based on the Kirkwood–Riseman theory[22,23]) the hydrodynamic ratio is a function of the fractal dimension of the aggregate *only*, so that there is no information on the crossover to the asymptotic region, in other words on the question how large the fractal aggregates have to be in order that the hydrodynamic ratio approaches the asymptotic value (as discussed below, this approach is slow for polymers in a good solvent[24])). The porous sphere approximation [26–28]) does give an idea of this finite size effect, and also allows us to investigate the influence of the finite width of the active growth zone. Our results suggest that the latter effect is small, but that finite size effects may reduce the hydrodynamic ratio by a factor of the order of 20% for aggregates of the size studied by Wiltzius.

The Kirkwood–Riseman theory[22,23]) and the porous sphere model of Debye and Bueche[26,27]) and Brinkman[28]) were introduced at the same time in the theory of the viscosity of polymer solutions, and our discussion will therefore illustrate in a very simple way many of the differences between these two approaches that have also emerged in that field[27,29]). As mentioned earlier, for polymers it has been known for quite some time[24]) that the Kirkwood–Riseman theory[22,23]) predicts $R_H \propto R_G$. Experimentally, however, R_H of polymers in good solvents is found to increase with a slightly different power of the degree of polymerization index N than R_G [24]). Weill and des Cloizeaux[30,24]) have suggested that this is due to a very slow crossover to the asymptotic regime, but it is difficult to obtain explicit predictions for R_H from the Kirkwood–Riseman theory[22,23]). In the porous sphere model[26–28]), on the other hand, the crossover is quite naturally included, and using this model together with independent data on the permeability of polymer solutions, Mijnlieff and Wiegel[29]) have been able to predict the viscosity and R_H without adjustable parameters to within 10 to 20%. The present approach to the hydrodynamic ratio of rigid fractal aggregates can be viewed as the complement of their application of the porous sphere model to flexible polymers in solution.

Understanding the growth of fractal aggregates on a fundamental level has turned out to be an extremely difficult problem. Similarly, it appears that the hydrodynamic radius of fractal aggregates cannot be predicted as easily as the above discussion may have suggested. Indeed, in reality, fractal aggregates are not characterized by a single fractal exponent, but rather by a distribution of exponents, e.g. the $f(\alpha)$ of Halsey et al.[31]). Meakin and Deutch[32]) have shown that the hydrodynamic forces on the particles in an aggregate follow similar scaling laws, and we therefore believe that R_H should in principle be a function of the full distribution $f(\alpha)$. To our knowledge, it is not sufficiently understood which factors are important in determining R_H, but we will nevertheless attempt to give a somewhat intuitive discussion of this, as it is the aim of this paper to guide experimental interpretation and to stimulate further experimental and theoretical research.

In section 2, we will first summarize the predictions of the Kirkwood–Riseman theory[22,23]) and estimate the accuracy of its prediction for the hydrodynamic ratio. After presenting the results of the porous sphere model[26–28]) in section 3, we then discuss in section 4 the possible effects of the asymmetry of the clusters, and the prospects for settling some of the issues raised by additional experiments.

2. Summary of the Kirkwood–Riseman results

The starting point of the Kirkwood–Riseman theory[22,23]) is the Oseen expression for the hydrodynamic interaction of two segments i and j of the system[33]); if, as in our case, the structure consists of spheres of equal size a, the hydrodynamic mobility tensor in this approximation is for $i \neq j$ given by[34]) $\mu_{ij} = (8\pi\eta r_{ij})^{-1}(\mathbf{1} + \hat{r}_{ij}\hat{r}_{ij})$. Here $\mathbf{1}$ is the unit matrix and $\hat{r}_{ij}$ a unit vector pointing from sphere i to j and η the fluid viscosity. Next, the diffusion coefficient is approximated by first performing a "preaverage", i.e. by assuming the angle between $\hat{r}_{ij}$ and some fixed direction is uniformly distributed, so that upon performing the angular average $\langle\ \rangle_a$ one gets $\langle \mu_{ij} \rangle_a = (8\pi\eta r_{ij})^{-1}(\mathbf{1} + \langle \hat{r}_{ij}\hat{r}_{ij} \rangle_a) = \mathbf{1}(6\pi\eta r_{ij})^{-1}$. This, of course, is an approximation since, when particle i is close to the perimeter of the structure, the angle is not at all uniformly distributed. Since the preaveraging has made the mobility tensor diagonal, one can then apply the Einstein relation $D = k_B T \langle \mu_{ij} \rangle$ to get (in the strong screening limit, the Stokes term for $i = j$ is neglected)

$$D = \frac{k_B T}{6\pi\eta}\left\langle \frac{1}{r_{ij}} \right\rangle = \frac{k_B T}{6\pi\eta} \frac{\int \mathrm{d}r\, r g(r)}{\int \mathrm{d}r\, r^2 g(r)}\,, \tag{1}$$

where $g(r)$ is the particle pair correlation function. With R_H of the aggregate defined through $D = k_B T/6\pi\eta R_H$, we thus get in this approximation[10,21,24])

$$R_H = \frac{\int dr\, r^2 g(r)}{\int dr\, r g(r)} . \tag{2}$$

Since $g(r)$ will be a scaling function of the form $g(r/R_G)$, we see that (2) indeed predicts that $R_H \propto R_G$. However, (2) also shows that when the fractal dimension is not too small, so that $g(r)$ does not drop off too fast, R_H is dominated by the large r behavior of $g(r)$. This behavior depends much less on the short range fractal structure of the aggregate than on the details of the growth conditions, however! To see this, note e.g. that when the aggregate forms a three dimensional ($d_f = 3$) spherical object of radius R_c, $g(r)$ is proportional to the overlap function for two spheres of radius R_c [35]),

$$g\left(\frac{r}{R_c}\right) \propto 1 - \frac{3}{4}\frac{r}{R_c} + \frac{1}{16}\left(\frac{r}{R_c}\right)^3 , \quad r \leq 2R_c . \tag{3}$$

This function drops off linearly for small r and vanishes quadratically at $r = 2R_c$ (the diameter of the sphere). The generalization of this result to fractal dimensions less than 3 is hampered by the fact that an aggregate is not fractal on large scales (of the order of the radius of gyration) and that there are correlations associated with the fact that the cluster grew out from some special point, the center[36–38]). As a result, to compute $g(r)$ one actually needs[38]) a three particle correlation function! One can derive an approximate expression neglecting this effect, but the results are cumbersome and hard to work with. This will therefore not be given here.

In passing, we note that when (3) is used in (2), one finds $R_H = \frac{5}{6}R_c$, while for a densely packed spherical aggregate with $d_f = 3$ one would, of course, expect R_H to be extremely close to R_c. This difference gives an idea of the error introduced by the "preaveraging" in the Kirkwood–Riseman theory[22,23]).

For the radius of gyration R_G, there are two equivalent expressions: in terms of $\rho(r)$, which gives the mass density at a distance r from the center of mass, R_G reads

$$R_G^2 = \frac{\int dr\, r^4 \rho(r)}{\int dr\, r^2 \rho(r)} , \tag{4}$$

but an alternative expression based on $g(r)$ is [39])

$$R_{\mathrm{G}}^2 = \frac{1}{2} \frac{\int \mathrm{d}r\, r^4 g(r)}{\int \mathrm{d}r\, r^2 g(r)} . \tag{5}$$

In principle, (4) is to be preferred, since $\rho(r)$ is much better known than $g(r)$ [when $d_{\mathrm{f}} = 3$, the equivalence of (4) and (5) can be checked with the aid of (3)]. However, since R_{H} in the Kirkwood–Riseman theory[22,23]) is expressed in terms of $g(r)$, one might hope that the errors made in an approximation of $g(r)$ partly cancel if (5) is used instead of (4), so that together with (2)

$$\frac{R_{\mathrm{H}}}{R_{\mathrm{G}}} = \frac{\int \mathrm{d}r\, r^2 g(r)}{\int \mathrm{d}r\, r g(r)} \left(\frac{2\int \mathrm{d}r\, r^2 g(r)}{\int \mathrm{d}r\, r^4 g(r)} \right)^{1/2} . \tag{6}$$

This is the expression used by Wiltzius[10]). The idea that the errors in (6) partly cancel is indeed borne out for $d_{\mathrm{f}} = 3$ for the approximation $g(r) \simeq \rho(r)$ considered by Wiltzius[10]) and implicitly by Hess et al.[21]), with $\rho(r)$ the mass density distribution with a sharp cutoff,

$$\begin{aligned} \rho(r) &= c r^{d_{\mathrm{f}}-3} , & r &< R_{\mathrm{c}} , \\ \rho(r) &= 0 , & r &> R_{\mathrm{c}} . \end{aligned} \tag{7}$$

When $d_{\mathrm{f}} = 3$, eq. (6) with $g(r) \simeq \rho(r) = \text{constant}$ yields $R_{\mathrm{H}}/R_{\mathrm{G}} = \sqrt{40/27} \simeq 1.22$, which is close to the exact value for a dense aggregate with $d_{\mathrm{f}} = 3$, $R_{\mathrm{H}}/R_{\mathrm{G}} = \sqrt{5/3} \simeq 1.29$. However, when d_{f} is substantially less than 3, we see no reason why this approximation should be accurate: when we approximate $g(r) \simeq \rho(r)$ but use (5) instead of (4), we underestimate for no good reason R_{G} by a constant factor $1/\sqrt{2} \simeq 0.7$, whereas (2) on the other hand gives with (7) and $g(r) \simeq \rho(r)$

$$R_{\mathrm{H}} = \frac{d_{\mathrm{f}} - 1}{d_{\mathrm{f}}} R_{\mathrm{c}} , \tag{8}$$

so that R_{H} in this approximation is a rapidly decreasing function of d_{f}. We believe that this result strongly underestimates the screening of hydrodynamic interactions for aggregates with smaller d_{f}. While a more detailed analysis of this will be given in section 3, our arguments can be illustrated in an intuitive way as follows.

For DLA clusters with $d_f \simeq 1.72$ in two dimensions, the width of the active zone is about $R_c/6$ (taking Meakin and Sander's[20]) mean deposition radius equal to R_c). Thus the Laplace field describing the diffusion of the particles forming the cluster is essentially screened from an interior region of the cluster with a radius of about $\frac{5}{6}R_c$. If the width of the active zone is about the same in three dimensions (we have not been able to find precise data for the thickness of the growth zone in three dimensions), one would expect $R_H \gtrsim \frac{5}{6}R_c$. Eq. (8), on the other hand, predicts $R_H \simeq 0.42\, R_c$ for a fractal with $d_f = 1.72$.

The above discussion also points at another problem of the Kirkwood–Riseman theory[22,23]): according to eq. (8), the hydrodynamic radius is a function of the fractal dimension of the aggregate only, whereas on physical grounds one would expect the degree of screening, and hence R_H, to depend rather on the width of the growth zone (which, implicitly, might be a function of d_f) and possibly on the size of the aggregate. As we now show, these effects are naturally included in the porous sphere model.

3. Results for the porous sphere model

In this section, we will assume that the fractal structures consist of spheres of size a, and that they can be reasonably well approximated by a spherically symmetric mass density distribution $\rho(r)$ of a form consistent with the scaling of the active growth zone with the radius of gyration,

$$\rho(r) = \rho_0 \left(\frac{r}{a}\right)^{d_f - 3} h(r/R_c)\,. \tag{9}$$

We take $h(0) = 1$ and $h(r/R_c) = 0$ for $r > R_c$, so that R_c is the largest radius at which the aggregate has nonzero mass; we have normalized $\rho(r)$ such that $\rho(a) = \rho_0$. The typical picture of the aggregate that we will have in mind is that of a three-dimensional generalization of the "dense branching morphology" found in electrodeposition experiments[40,41]).

In the porous model, an aggregate consisting of spheres with radius a is, at a distance r from the origin, essentially considered as a porous medium with local permeability $(6\pi a\rho(r))^{-1}$; according to the Debye–Bueche–Brinkman[26–28]) equation, the fluid flow velocity $\boldsymbol{v}$ around the fixed structure is then given by

$$\eta\nabla^2\boldsymbol{v} - 6\pi\eta a\rho(r)\boldsymbol{v} - \boldsymbol{\nabla}p = \boldsymbol{0}\,, \qquad \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0\,, \tag{10}$$

where p is the pressure. A short intuitive deviation of this equation has been given by Wiegel and Mijnlieff[42]), while Felderhof and Deutch[43]) have shown that by treating the hydrodynamic interactions in the Oseen approximation

(10) is indeed obtained in the mean field limit for a system of density $\rho(r)$ of spheres of size a. Thus, the starting point for the treatment of the hydrodynamic interactions is the same as in the Kirkwood–Riseman[22,23]) approximation, but the "preaveraging" is replaced by a mean field limit. As a result, the central quantity in the porous sphere approximation is $\rho(r)$ rather than $g(r)$, which, as we have discussed, has some advantages for fractal aggregates.

It is convenient to use dimensionless units by writing distances in units of R_c. In these units the fractal occupies the region $r \leqslant 1$, and (10) becomes

$$\nabla^2 \boldsymbol{v} - \mu(r)\boldsymbol{v} - \frac{1}{\eta}\nabla p = \boldsymbol{0}\,, \qquad \nabla \cdot \boldsymbol{v} = 0\,, \tag{11}$$

where (9) and (10) yield

$$\mu(r) = (6\pi a^3 \rho_0)\left[\frac{R_c}{a}\right]^{d_f - 1} r^{d_f - 3} h(r)\,. \tag{12}$$

The most important physics in (11) is that the screening of the hydrodynamic field increases with μ, and (12) shows that as $R_c \to \infty$, $\mu \to \infty$ for all $r < 1$ and $d_f > 1$ (in agreement with Witten's argument[18])). This implies that in this approximation the hydrodynamic field gets more and more expelled from the interior of the aggregate, so that the hydrodynamic radius approaches that of a sphere of radius R_c,

$$R_H \to R_c \quad (R_c \to \infty)\,. \tag{13}$$

This result lends support to the claim made earlier that approaches based on the Kirkwood–Riseman theory[22,23]) obtained hydrodynamic radii which are much too small (in particular for smaller d_f).

While according to (13) the asymptotic value of R_H is independent of d_f, the crossover to this value is obviously not, and we now discuss the influence on R_H of the most important factors affecting the magnitude and r dependence of $\mu(r)$. To do so, we have used some results related to a Faxén theorem for (11). For an impenetrable spherical particle, the Faxén theorems[7–9]) express the force and torque on the particle in terms of averages of the unperturbed but arbitrary flow over the surface and volume of the sphere. The generalization of these results to the porous sphere model is due to Felderhof and Jones[44]). Their results[45]) allow us to calculate R_H from the asymptotic behavior of two functions ϕ and ψ which are related to the velocity and pressure field, but which for arbitrary $\mu(r)$ have to be obtained numerically from a set of *ordinary* differential equations. Our computer program uses the NAG routine D02TGF to solve these equations. We now discuss our results.

Although $\mu(r)$ has a weak divergence at the origin, this divergence plays hardly any role when R_c is not too small. This is because for realistic values of R_c the velocity field is already screened completely from the center in the absence of this divergence. Furthermore, since fractal aggregates typically have a relatively thin growth zone, we expect $h(r)$ to be substantially different from 1 only for r close to 1. This suggests that a useful approximation to study the finite size dependence is to put

$$\mu(r) = \begin{cases} \kappa \equiv (6\pi a^3 \rho_0)\left[\dfrac{R_c}{a}\right]^{d_f - 1}, & r < 1, \\ 0, & r > 1. \end{cases} \tag{14}$$

In this approximation the model reduces to that of a uniformly porous sphere, and can be solved analytically. The resulting expression for R_H (in dimensional units) is[27,44])

$$R_H = R_c \frac{1 - \kappa^{-1/2} \tanh \kappa^{1/2}}{1 + \frac{3}{2}\kappa^{-1} - \frac{3}{2}\kappa^{-3/2} \tanh \kappa^{1/2}}, \tag{15}$$

and this behavior is sketched in fig. 1. To estimate the value of κ in Wiltzius' experiments[10]), we note that the factor $6\pi a^3 \rho_0$ is expected to be of order unity, since there will typically be one or a few particles at a distance $2a$ from the center, so that ρ_0 is of order $1/[\frac{4}{3}\pi(2a)^3]$. Using therefore $\kappa \simeq (R_c/a)^{d_f - 1}$, we find that κ varies from about 20 to 200 over the range where the data scale as

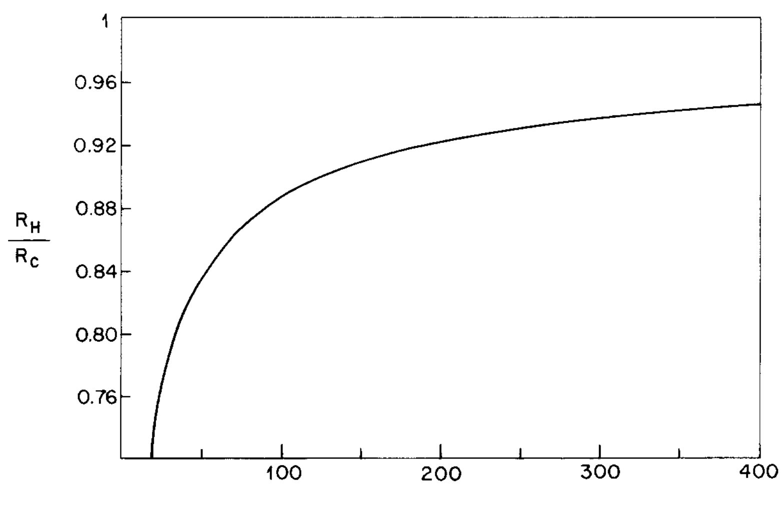

Fig. 1. R_H/R_c of a sphere for uniform porosity. κ is the inverse permeability defined in eq. (14).

expected [$700 \leqslant R_G \leqslant 7000$ Å, $q \simeq 70$ Å, $R_G \simeq 0.7R_c$]. Thus, in this range, we estimate that there still is a noticeable finite size effect, with R_H increasing from $0.73R_c$ to $0.92R_H$.

As discussed earlier, we expect the d_f dependence of R_H through the term r^{d_f-3} in (12) to be quite small. We have checked this numerically, and found this indeed to be the case. For example, taking this term into account for $d_f = 2$ and $\kappa = 20$ changes R_H by only about 2%. For larger values of κ, the term has even much less effect on R_H.

Obviously, the effect of $h(r)$ in (12) on R_H will depend on the precise form of the function $h(r)$ on R_H. Since the growth of fractal aggregates takes place at an outer growth zone, we expect that $h(r)$ will typically be close to unity in the interior of the fractal and then drop rapidly to zero in the growth zone. We have modeled such behavior with two different *ad hoc* expressions for $h(r)$: a piecewise linear function,

$$h(r) = \begin{cases} 1\,, & r < 1 - \eta\,, \\ 1 - \eta^{-1}(r - 1 + \eta)\,, & 1 - \eta < r < 1\,, \end{cases} \tag{16}$$

and a function that varies quadratically for $r > 1 - \eta$,

$$h(r) = \begin{cases} 1\,, & r < 1 - \eta\,, \\ 1 - 2\eta^{-2}(r - 1 + \eta)^2\,, & 1 - \eta < r < 1 - \eta/2\,, \\ 2\eta^{-2}(r - 1)^2\,, & 1 - \eta/2 < r < 1\,. \end{cases} \tag{17}$$

R_H will clearly be reduced by an increase in the width of the growth zone. However, an increase in the width of the growth zone also implies a decrease in R_G, since the mass distribution is then more biased towards the interior region. It is therefore more useful to plot the hydrodynamic ratio R_H/R_G directly, since its η dependence will be smaller than that of R_H and R_G separately. Indeed, fig. 2 shows that the change in the ratio with η for $\kappa \simeq 100$ is so small for moderate values of η (as mentioned earlier, $\eta \simeq \frac{1}{6}$ for two dimensional DLA clusters[20])) that one may for all practical purposes neglect it completely.

We note, however, that according to (12) $R_H \to R_c$ in the limit of infinite R_c, independent of η. As a result, for extremely large values of κ, the near cancellation of the η dependence of R_H and R_c will not occur. However, this disappearance of the η dependence from R_H for $\kappa \to \infty$ is probably an incorrect result of the present approximation. The thickness of the growth zone scales with R_c, and one therefore physically expects the hydrodynamic field to penetrate the fractal over a distance of order of the growth zone, irrespective of the size. Presumably, the large κ scaling properties of the present model are

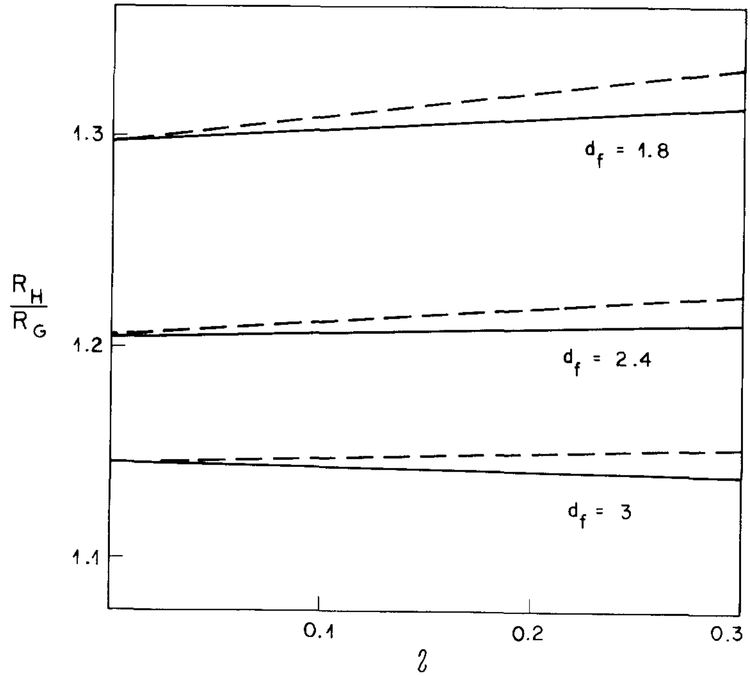

Fig. 2. The hydrodynamic ratio R_H/R_G for $\kappa = 100$ and three values of d_f. The solid lines correspond to the function $h(r)$ given by (16) and the dashed lines to $h(r)$ given by (15).

incorrect since it is based on a mean field approximation [see the discussion following (10)].

The above discussion shows that within our approach the hydrodynamic ratio is well approximated by using for R_H the expression (15) for a sphere of uniform porosity, and for R_G the result $R_G = \sqrt{d_f/(d_f+2)}R_c$, valid for a mass distribution $\rho(r)$ with a sharp cutoff [cf. eqs. (4) and (7)]. Thus within the present model our final expression, accurate even for fractals without a sharp cutoff, is

$$\frac{R_H}{R_G} = \left(\frac{d_f+2}{d_f}\right)^{1/2} \frac{1-\kappa^{-1/2}\tanh\kappa^{1/2}}{1+\frac{3}{2}\kappa^{-1}-\frac{3}{2}\kappa^{-3/2}\tanh\kappa^{1/2}}\,, \tag{18}$$

with κ defined in (14). According to the first factor, R_H/R_G *increases* with decreasing d_f because R_G becomes smaller, while the second term has an opposite effect since for N fixed, κ decreases with decreasing d_f (κ scales as $N^{(d_f-1)/d_f}$, with N the number of units in the cluster). This behavior is different from that of the Kirkwood–Riseman approximation[22,23]), in which R_H/R_G always *decreases* because of the strong d_f dependence of R_H.

For $d_f = 2.07$, the value measured by Wiltzius[10]), the porous sphere model yields as a typical value $R_H/R_G \simeq 1.23$ (taking $\kappa \simeq 100$). This value is a factor 1.7 larger than the experimental value given by Wiltzius[10]), and only about 0.7 of the value he quotes from unpublished numerical work by Meakin[25]). In the next section, we will discuss this in more detail and make suggestions for sorting out these discrepancies experimentally as well as numerically.

4. Discussion of results and suggestions for further experiments

Let us now try to understand the possible origin of the differences between the various values for the hydrodynamic ratio, 0.72 (experimental), 1.23 (porous sphere model) and 1.75 (numerical simulations for an aggregation model with a different d_f). We will not discuss any further the results of the Kirkwood–Riseman[22,23]) approximation, since it was already argued in section 2 that these should be considered unreliable.

As is well known, most fractals are not sufficiently characterized by their fractal dimension – in principle a whole distribution of exponents is needed (the $f(\alpha)$ of Halsey et al.[31]) – but to our knowledge such a quantity cannot yet be measured experimentally for fractal aggregates, and neither do we know how to compute R_H from it, other than by direct numerical simulations[32]). The best we can therefore do at present is to offer some speculative explanations, in the hope that this will stimulate further research on this question.

The porous sphere model obviously will work best for fractal aggregates whose mass distribution is nearly spherical and has a relatively well defined cutoff (we stress, however, that the discussion in section 3 shows that the result (18) is also accurate if the cutoff is not completely sharp). Such fractals have been observed in two-dimensional electrodeposition experiments[40,41]) (the "dense branching morphology"[41]). We believe that if three-dimensional generalizations of such fractals would exist the porous sphere model would yield a fair prediction for their hydrodynamic radius. Indeed, using this model and independent porosity data, Mijnlieff and Wiegel[29]) calculated the viscosity and R_H of polymers in solution without any adjustable parameters, and their results agree to within 10 to 20% with the experimental values.

In reality, most fractal objects are not at all spherically symmetric – they often consist of several pronounced branches (cf. e.g. fig. 3a of ref. 40) with large gaps of the order of the radius of gyration in between the branches – and even if they are rather homogeneous, their overall shape can still be quite asymmetric. As we will argue, both features may have a large effect on R_H.

Clearly, it is desirable to have more detailed numerical studies of R_H of simulated clusters. The value 1.75 for R_H/R_G attributed by Wiltzius[10]) to unpublished work by Meakin[25]) is quite a bit larger than our estimates (the porous sphere model gives $R_H/R_G \approx \sqrt{3} = 1.7$ only in the limit of very large aggregates with d_f near 1). Such a large value of R_H/R_G is a sign that the fractal cannot be modeled by a spherically symmetric mass density $\rho(r)$. For, our asymptotic result $R_H \to R_c$ *certainly* yields an upper bound for R_H for spherically symmetric clusters; although R_G does decrease somewhat if the width of the growth zone increases, we do not expect this effect to be too large [both for eq. (16) and eq. (17), we have to first order in η $R_G = \sqrt{d_f/(d_f+2)}(1-\eta/2)$]. Thus, it is very unlikely that aggregates with a spherically symmetric $\rho(r)$ can have hydrodynamic ratios larger than the $\kappa \to \infty$ value $\sqrt{(d_f+2)/d_f}$. If the value 1.75 from the simulations is correct, I consider it likely that the apparent "enhancement" of R_H is due to the branch structure that may dominate the outer region of fractal objects. Such branches will correspond to a large R_H, since they are unscreened and so quite exposed to the flow field. An alternative way to think about this is that the spherically symmetric aggregate has much more mass at the outer perimeter than is necessary to have R_H close to R_c (the radius beyond which ρ vanishes). If this is true, an aggregate with a larger hydrodynamic ratio can be created by cutting away some pieces from the outer region of a nicely spherically symmetric aggregate, as this will reduce R_H only slightly but R_G significantly. Our ideas regarding these general trends can, of course, suitably be tested through simulations, and we hope that this will be done in the future. Another aspect that can usefully be investigated with simulations is the effect of the correction term to the Oseen approximation for the hydrodynamic interactions, which are neglected in the analytical approaches[22,23,26–28,43]) but retained in the numerical evaluations of R_H [13,14,32]). However, such correction terms cannot lead to significantly larger values of R_H for spherically symmetric clusters, since R_c is an upper bound to R_H.

Fractal clusters and aggregates are generally quite asymmetric. To our knowledge, this has only been demonstrated quantitatively for lattice animals and several percolation clusters[47]), but a glance at the TEM images of Weitz and Lin[48]) show that aggregates similar to those studied by Wiltzius[10]) (both have a fractal dimension consistent with the reaction limited cluster–cluster aggregation models) have a substantial anisotropy too: the long axes of the two-dimensional images appear to be roughly a factor of two larger than the short ones.

Can asymmetry explain the small value of R_H/R_G measured by Wiltzius[10])? At first sight, the answer appears to be no, since R_H/R_G has been calculated for prolate and oblate ellipsoids of revolution by Perrin[49]). As discussed by

Wiltzius[10]), his results imply only a small (7%) reduction of the hydrodynamic ratio for prolate ellipsoids or revolution with an axis ratio of 2, while the experimental value is some 40% smaller than our estimate. However, on closer inspection it appears that this suggestion deserves further attention.

The diffusion coefficient of ellipsoids calculated by Perrin[49]) is the *long time* diffusion coefficient. On time scales much longer than the rotational relaxation time, even the diffusion of an asymmetric particle is isotropic, since any short time anisotropies are averaged out by the constant reorientation of the particle due to Brownian motion. On time scales shorter than the rotational relaxation time, however, the diffusion of an asymmetric paticle will be very anisotropic: its friction coefficient along the long axis is typically smaller than that perpendicular to that axis (see, e.g. Happel and Brenner[33]) for the relevant expression for ellipsoids of revolution), and hence its diffusion coefficient along this axis is enhanced.

The rotational relaxation time τ_r for a sphere of radius a is[33,39]) $\tau_r = 8\pi\eta a^3/kT$. In line with our conclusion that a large fractal aggregate can be considered as an impenetrable sphere, the results of Felderhof and Jones[44]) show that the rotational relaxation time τ_r similarly will be of order $8\pi\eta R_H^3/kT$ (anisotropy of the aggregate would enhance the relaxation time; see, e.g., Berne and Pecora[39])). In the quasi-elastic light scattering experiments, the scattering intensity at wavevector $\boldsymbol{q}$ decays as

$$e^{-Dq^2t} = e^{-(kT/6\pi\eta R_H)q^2t} \simeq e^{-q^2R_H^2t/\tau_r} . \tag{19}$$

Thus, it is clear that such experiments will probe essentially the long time diffusion if $q^2R_H^2 \lesssim 1$ and the anisotropic diffusion if $q^2R_H^2 \gtrsim 1$.

In Wiltzius' experiments[10]), the scattering wavevector q ranges from $2.6 \times 10^4\ \text{cm}^{-1}$ to $2.6 \times 10^5\ \text{cm}^{-1}$, and as a result for the largest aggregates observed ($R_H \simeq 7000$ Å) $q^2R_H^2$ ranges between 3.2 and 320. Since the aggregates appear to be quite asymmetric, I therefore expect that the diffusion of the largest clusters is anisotropic. Although the aggregates will be oriented randomly with respect to the scattering vector $\boldsymbol{q}$, it is conceivable that the initial decay of the scattering intensity is dominated by those aggregates whose diffusion coefficient along the direction of $\boldsymbol{q}$ is large, i.e. whose effective hydrodynamic radius in that direction is small. This would obviously lead to a smaller apparent R_H. Given the indications of a strong asymmetry and the fact that the R_G is increased by asymmetry of the aggregates, a substantial reduction of the hydrodynamic ratio R_H/R_G seems possible. Unfortunately, in order to make these ideas more quantitative, a better understanding is needed of the effect of anisotropic diffusion on the time dependence of the scattering intensity, as well as of the aggregate asymmetry.

The data of Wiltzius[10]) also include aggregates for which $q^2R_H \lesssim 1$ throughout most of the range of q values. For these aggregates, the isotropic diffusion will be measured. However, these smaller aggregates also correspond to a smaller value κ [cf. eq. (12)] and hence finite size effects might be partially responsible for the small values of R_H/R_G of these fractals.

We stress that the above suggestions are very tentative, but we feel that they are worth testing. Apart from reanalyzing the data and performing numerical simulations, there are several interesting experiments that would bear on the issue of assymetry and anisotropy of the aggregates. In particular, measurements of the rotational relaxation time of the sedimentation velocity yield different ways of obtaining the hydrodynamic radius. The effective hydrodynamic radius determined from the rotational relaxation time measurable with depolarized light scattering[39]) is dominated by the length of the longest axis of the aggregate[39]). Thus, if our suggestions regarding the effect of asymmetry are correct, the measurements of R_H through rotational relaxation should give higher values of R_H than diffusion measurements in the regime $q^2R_H^2 \gtrsim 1$. Similarly, in a sedimentation experiment one would measure the long time behavior, and hence the effective rotationally averaged R_H, which I would expect to lie between the values obtained from the other two experiments. We also mention that second order light scattering may yield useful additional information on the structure of aggregates, as pointed out recently by Chen et al.[50]).

Finally, we note that in practice the cluster size distribution in the reaction limited cluster aggregation regime falls off with a power law of the mass of the clusters up to some well-defined cutoff mass which grows exponentially in time[51]). Thus, the question arises whether the polydispersity could give rise to a smaller effective R_H. However, it is unclear why the static and quasi-elastic light scattering would be influenced differently by the polydispersity, and theoretical consideration[52]) confirms the idea that both are dominated by the largest clusters in the system, as if the clusters were monodisperse.

In conclusion, we have analyzed the hydrodynamic radius of fractal aggregates, and argued that the experimental value is considerably smaller than expected for spherically symmetric aggregates. We have therefore tentatively attributed the discrepancy to the asymmetry of the clusters, and suggested various ways to test this experimentally.

Acknowledgments

I would like to thank Alan Hurd and in particular Pierre Wiltzius for useful discussions and comments.

Note added in proof

After acceptance of this paper, it was pointed out by Chen et al.[53]) that the simulation result $R_H/R_G \approx 1.75$, which was communicated privately and to which we compared our results in this paper, is unfortunately incorrect. In their latest simulations of clusters of size $N \lesssim 400$, Chen et. al.[53]) find $R_H/R_G \approx 0.97$ for the reaction limited cluster aggregation model relevant for Wiltzius' experiment[10]). Since κ scales as $N^{(d_f-1)/d_f}$, a reasonable value for clusters of size $N \lesssim 400$ and $d_f \approx 2.1$ is $\kappa = 20$. With this value, the porous sphere model gives $R_H/R_G \approx 1.03$, which is quite close to the value found in the simulations. Nevertheless, this apparent agreement is somewhat fortuitous, since the precise value of κ is not known [see the discussion following eq. (15)]. We stress, however, that a detailed test of the porous sphere model can in fact be made with simulations like those of Chen et. al.[53]), since the effective value of κ in the simulations can be determined accurately from the data of the full mass particle distribution function. We hope that such a detailed comparison will be done in the future.

Furthermore, Pusey et al.[54]) have pointed out that since R_H and R_G are related to different moments of the cluster mass distribution, polydispersity reduces R_H/R_G. We refer to this comment[54]) and the reply by Wiltzius and the author[55]) for a discussion of whether finite size effects and polydispersity fully account for the discrepancies between theory and experiment.

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