Wiltzius and van Saarloo's Reply: In their Comment, Chen, Meakin, and Deutch present values for the ratio of the hydrodynamic radius $R_H$ to the radius of gyration $R_G$ for fractal aggregates. The values have been obtained for two important computer simulation models, diffusion- and reaction-limited cluster-cluster aggregation. For the latter model, the value $R_H/R_G$ is much closer to the experimental result $R_H/R_G = 0.72 \pm 0.02$ than is the ratio $1.75$ communicated in private earlier by Chen, Meakin, and Deutch. Pusey et al. show that if, in addition, the effects of polydispersity are taken into account, one obtains estimates for the ratio $R_H/R_G$ that cluster around the experimental value. We are pleased with the contributions made in both Comments. Nevertheless, it is our opinion that the comparison of theory and experiment is somewhat more complicated than might appear from the preceding Comments.

It is well known in polymer theory that $R_H$ and $R_G$ reach their asymptotic scaling behavior with slightly different powers of the degree of polymerization, giving rise to a notoriously slow crossover of $R_H/R_G$ to the true asymptotic value. This crossover is difficult to study within the Kirkwood-Riseman theory, but is naturally included in the porous-sphere model, in which a polymer or aggregate is treated as a sphere with porosity inversely proportional to the density of monomers. For the clusters studied by Chen, Meakin, and Deutch, the value $R_H/R_G \approx 1$ is in the range expected in the porous-sphere model for clusters of size $N \leq 400$ and $d_f \approx 2.1$. Experimentally, the ratio of clusters of about the same size ($R_G \approx 400$ Å) is also around unity. Hence, if these relatively small clusters of the same size are compared, polydispersity is not needed to account for the data. In general, one has to be cautious to apply polydispersity considerations based on asymptotic power-law cluster-size distributions to small clusters with $N \leq 400$.

Chen, Meakin, and Deutch unfortunately have no data for larger clusters. In the experiments, the measured value of $R_H/R_G$ decreases with cluster size, to reach its "asymptotic" value around $R_G \approx 800$ Å. The porous-sphere model, however, predicts an increase of $R_H/R_G$ with cluster size; and for $N$ of order $10^4$, relevant for the largest clusters studied experimentally, $R_H/R_G$ is predicted to be 20% larger than in the numerical simulations, whereas the experimental value is 30% smaller. Even when a reduction of order 20% to 30% due to polydispersity is taken into account, the theoretical estimates based on the porous-sphere model are somewhat larger than the value observed in this range.

An aspect neglected in both the Kirkwood-Riseman scheme and the Comments is aggregate anisotropy. Large-scale computer simulations of various aggregation models as well as number-fluctuation spectroscopy measurements on aggregating latex microspheres have indeed shown that the long axis of large clusters is roughly twice as long as the short axis. Such an asymmetry could also introduce a systematic reduction of $R_H/R_G$ as measured with light-scattering techniques in the range $500$ Å $\leq R_H \leq 7000$ Å. Additional complications for the theoretical treatment of the hydrodynamic behavior arise possibly from some flexibility in the periphery of the aggregates, although we do expect this effect to be small.

In conclusion, while we welcome the fact that the computer results and the theoretical analysis of polydispersity have brought the theory and the in situ experiments on colloidal aggregates into much closer agreement than was previously believed, we believe that the finite-size effects, polydispersity, and anisotropy of the clusters require further investigation, through, e.g., depolarized light scattering and sedimentation experiments.

Pierre Wiltzius and Wim van Saarloos
AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received 27 August 1987
PACS numbers: 61.25.Hq, 05.40.+j, 05.60.+w, 36.20.-r

---

6. See W. van Saarloos, Physica (Amsterdam) (to be published), and references therein.