Diffusion Coefficient for Fractal Aggregates

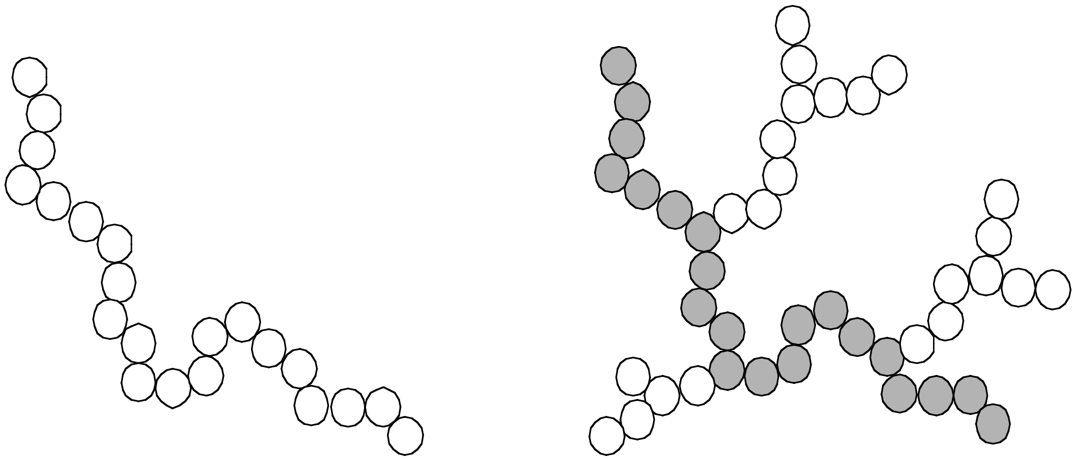

Figure 1 a) Linear aggregate and b) branched aggregate with minimum path in grey.

The diffusion coefficient for a spherical particle, D_1, in the continuum regime is given by the Stokes-Einstein equation,

$$D_1 = \frac{kT}{f_1} \; ; f_1 = 3\pi d_1 \eta_0 \tag{1}$$

where f_1 is the friction factor or drag coefficient such that the drag force if given by $F_{drag} = f_1 c$, where c is the sphere velocity, d_1 is the Sauter mean diameter and η_0 is the viscosity of the media. The diffusion coefficient, D_{agg}, for a linear chain, of size d_{agg}, under the free draining limit (Rouse behavior), Figure 1a, is,

$$f_{agg} = Nf_1 = \left(\frac{d_{agg}}{d_1}\right)^{d_f} f_1 \; ; D_{agg} = \left(\frac{d_1}{d_{agg}}\right)^{d_f} D_1 = \frac{D_1}{N} \tag{2}$$

where N is the degree of aggregation and d_f is the mass fractal dimension.

Alternatively, in the non-draining limit the aggregate is treated as a sphere of diameter d_{agg},

$$D_{agg} = \frac{D_1}{\left(d_{agg}/d_1\right)} = \frac{D_1}{\left(\alpha N^{1/d_f}\right)} \tag{3}$$

For a branched structure these two limits can be described by a single function if the fractal structure is considered in terms of the minimum path length, p, minimum dimension, d_{min}, and connectivity dimension, c. For the branched aggregate of figure 1b a path through the ramified structure, grey circles, is composed of p circles. This path, if considered independent of the branches, forms a fractal aggregate with dimension d_{min} so,

$$p = \beta \left(\frac{d_{agg}}{d_1} \right)^{d_{\min}} \tag{4}$$

where β is the lacunarity constant and is of the order of 1. Further, we have for the entire aggregate

$$N = \beta \left(\frac{d_{agg}}{d_1} \right)^{d_f} \tag{5}$$

So that,

$$N^{1/d_f} = p^{1/d_{\min}} \text{ or } N = p^{d_f/d_{\min}} = p^c \tag{6}.$$

The connectivity dimension c is 1 for a linear aggregate and d_f for a fully branched, regular aggregate.

In figure 1b the number of circles in branches is N-p and the mole fraction branches, ϕ_{Br}, is given by,

$$\phi_{Br} = \frac{N - p}{N} = 1 - N^{(1/c) - 1} \tag{7}$$

ϕ_{Br} can be considered a weighting factor for the extent of draining for the aggregate in that when $\phi_{Br} = 1$ the aggregate is by definition completely non-draining and when $\phi_{Br} = 0$ the aggregate is likely to be fully drained following Rouse behavior. We can generalize,

$$f_{agg} = f_1 \left(\phi_{Br} \alpha N^{1/d_f} + (1 - \phi_{Br}) N \right) = f_1 \left(\alpha N^{1/d_f} - \alpha N^{(1/c) + (1/d_f) - 1} + N^{1/c} \right) \tag{8}$$

where α = 1/β.

$$D_{agg} = \frac{kT}{f_{agg}} = D_1 \left(\alpha N^{1/d_f} - \alpha N^{(1/c) + (1/d_f) - 1} + N^{1/c} \right)^{-1} \tag{9}.$$

In the free-molecular regime the Epstein, PS (1924) Phys Rev 23 710 function can be substituted for Stokes Law for the single particle friction factor,

$$f_{1,FM} = \frac{2}{3} d_1^2 \rho \left(\frac{2\pi kT}{m} \right)^{1/2} \left[1 + \frac{\pi \alpha_1}{8} \right] \tag{10}.$$

where ρ is the media density, m is the molecular mass of gas molecules and α_1 is the accommodation coefficient describing the interaction of gas atoms with the particle.

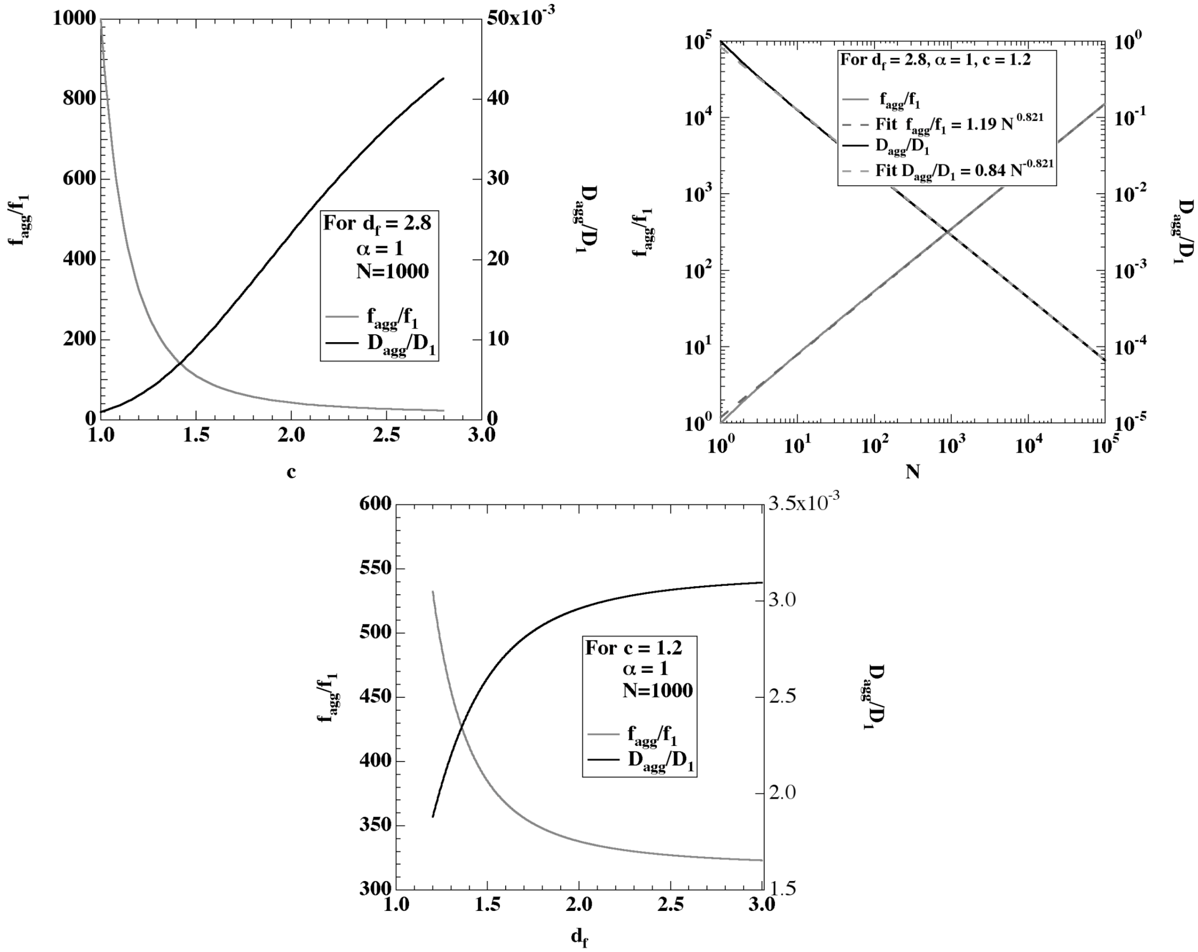

Figure 1. Friction factor f and diffusion coefficient D from equations (8) and (9) versus connectivity dimension c for aggregates of 1000 primary particles with a mass fractal dimension of 2.8. $c \le d_f$ by definition. a) Larger c reflects smaller aggregates with higher branch content at a constant overall N and d_f. b) A power-law dependence is seen at large N where $\frac{f_{agg}}{f_1} = cN^{1/c}$ and $\frac{D_{agg}}{D_1} = \frac{1}{c}N^{-1/c}$. This is true since 1/c is close to 1 in the second term of (8). c) Dependence of f and D on the mass fractal dimension. Larger d_f indicates denser and smaller size aggregates with a lower friction factor.