

## Sphere dynamics in isotropic colloidal rod fluids

G H Koenderink, A P Philipse<sup>†</sup> and S G J M Kluijtmans<sup>‡</sup>

Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Research Institute,  
Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received 10 September 1999

**Abstract.** Long-time self-diffusion and sedimentation of tracer spheres in dispersions of rigid colloidal host rods has been measured *in situ* as a function of rod volume fraction for various sphere and rod dimensions. The sphere friction factor, which was always the same for diffusion and sedimentation, is determined only by the macroscopic rod viscosity when the rods are relatively mobile (dilute regime). However, when the host-rod dynamics is slow (semi-dilute regime) the tracer friction is much smaller than expected from the host viscosity, and markedly dependent on the sphere/rod size ratio. These experiments on well defined rod–sphere mixtures, supported by low-shear rheology and birefringence measurements, confirm that current models for hindered tracer dynamics do not (adequately) incorporate host mobility.

### 1. Introduction

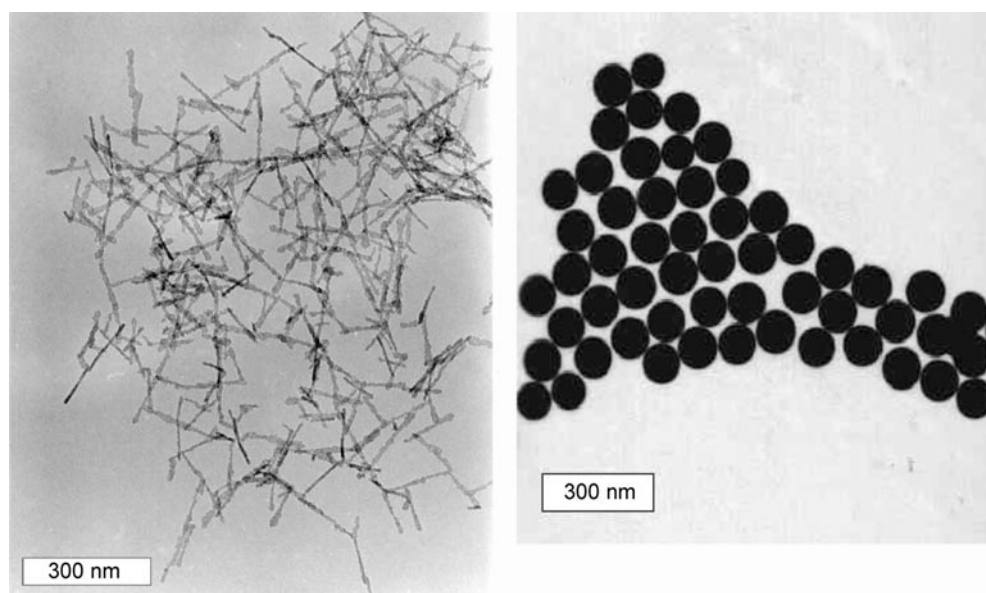
Hindered diffusion of colloidal tracer spheres has been studied in our group for the case of tracer spheres in *static* confining geometries. Examples are diffusion of silica colloids in transparent glasses with a bicontinuous pore structure [1, 2] and in random sphere packings [3]. Recently we have explored tracer-sphere dynamics in hindering media containing *thermal* host particles, in particular rigid Brownian rods. One main issue we try to resolve (experimentally) is how the friction factor in tracer diffusion and sedimentation depends on the tracer size, and the concentration and size of the host rods. This contribution summarizes some first results for the dynamics of fluorescent silica tracer spheres, measured *in situ* in dispersions of silica rods. Details of experimental procedures and more elaborate discussions can be found in [4].

### 2. Experiment

Dimensions of the colloids (figure 1) are listed in tables 1 and 2. The host rods are rigid silica rods with a controllable size and aspect ratio [5–7]. The tracers are silica spheres labelled with a fluorescent core [8]. The charged silica spheres and rods are dispersed in a  $10^{-3}$  M solution of LiCl in DMF (dimethylformamide) to form stable, non-aggregated mixtures. The refractive index of DMF ( $n = 1.43$ ) nearly matches that of silica ( $n = 1.45$ ) so the silica is optically nearly transparent. This allows *in situ* measurement of the long-time self-diffusion with FRAP (fluorescence recovery after photobleaching [9]), making use of the fluorescent cores. Typical diffusion distances probed are 5 to 20 microns. The tracer cores

<sup>†</sup> Corresponding author.

<sup>‡</sup> Present address: Fuji Photo Film, Tilburg Research Laboratory, Oudenstaart 1, PO Box 90156, 5000 LJ, Tilburg, The Netherlands.



**Figure 1.** TEM photographs of colloidal host rods L100 and of fluorescent tracer spheres D740.

**Table 1.** Number average length ( $L$ ) and diameter ( $D$ ) of L100 and L200 silica rods, determined by digital image analysis of electron micrographs (see figure 1).

System code	$L$ (nm)	$D$ (nm)	$L/D$
L100	$101.9 \pm 39.7$	$10.6 \pm 3.3$	9.6
L200	$228.9 \pm 88.9$	$8.9 \pm 2.0$	25.7

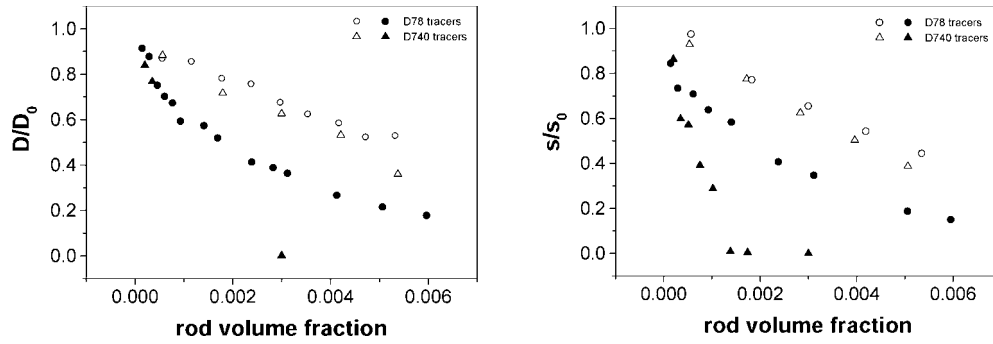
**Table 2.** Radius of silica tracer spheres D78 and D740, determined from electron micrographs ( $R_{TEM}$ ) and from dynamic light scattering experiments ( $R_{DLS}$ ).

System code	$R_{TEM}$ (nm)	$R_{DLS}$ (nm)
D78	$32 \pm 3$	$39 \pm 1$
D740	$344 \pm 33$	$370 \pm 8$

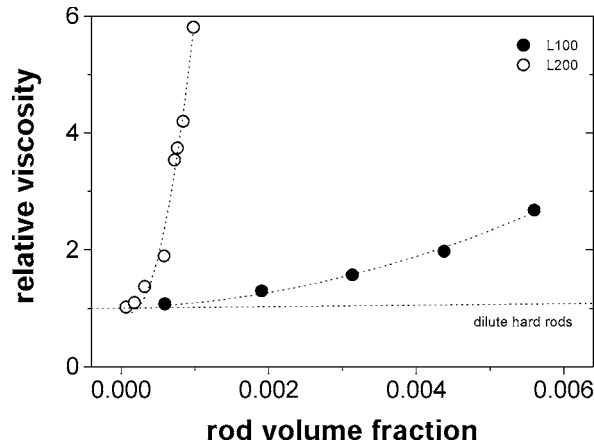
can also be used to detect sedimentation of tracer spheres in dispersions of non-sedimenting rods with an analytical ultracentrifuge. The high reproducibility of sedimentation results, among other things, confirms the absence of aggregation or clustering in the sphere-rod mixtures. The host-rod suspensions were investigated separately by dynamic light scattering, low-shear rheology and birefringence relaxation to obtain information about the translational and rotational mobilities of the rods [4].

### 3. Results and discussion

Results for tracer-sphere diffusion and sedimentation at various host-rod volume fractions are shown in figure 2. Striking are the very low rod concentrations at which tracer mobility is already hindered, sometimes up to the point of complete sphere arrest. This arrest, for purely repulsive particles, implies permanent ‘caging’ of a tracer sphere by an immobile, entangled



**Figure 2.** Reduced diffusion (left) and sedimentation (right) coefficients of the D78 and D740 silica tracer spheres in dispersions of L100 (open symbols) and L200 (closed symbols) rods.



**Figure 3.** Relative low-shear viscosity of dispersions of short (L100) and long (L200) rods in DMF ( $10^{-3}$  M LiCl) as a function of the rod volume fraction.

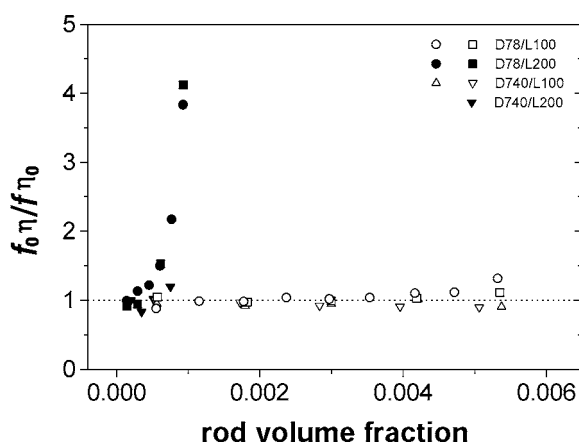
structure of rigid rods [10]. Conversely, from a finite long-time tracer self-diffusion in figure 2 we cannot conclude that rods must be mobile, because a sufficiently small tracer may penetrate a static rod network. A better indicator for a mobile host-rod dispersion is an effective dispersion viscosity  $\eta(\varphi)$  in the diffusion coefficient  $D$  and sedimentation coefficient  $s$  of a tracer sphere with diameter  $\sigma$ :

$$D = \frac{kT}{3\pi\eta(\varphi)\sigma} \quad (1)$$

$$s = \frac{m}{3\pi\eta(\varphi)\sigma}. \quad (2)$$

Here  $\varphi$  is the volume fraction of rods and  $m$  the effective tracer mass.  $D_0$  and  $s_0$  are the coefficients for a free tracer in a solvent with viscosity  $\eta_0$ . The ratios  $D\eta/D_0\eta_0$  and  $s\eta/s_0\eta_0$  equal unity if the tracer friction is determined by the (low-shear) viscosity of the rod suspension.

Figure 3 shows the low-shear viscosity results for the rods, which are combined in figure 4 with the data from figure 2. We find that an effective Stokes friction indeed applies for nearly the whole measured volume fraction range of the shorter host rods L100 (table 1) irrespective of the tracer size. On the other hand, for the longer host rods L200 we observe a marked



**Figure 4.** Product  $f_0 \eta / f \eta_0$  versus rod volume fraction, with  $f$  the friction factor—determined either from diffusion results (circles, up triangles) or from sedimentation results (squares, down triangles)—for tracer diffusion in L100 (open symbols) and L200 (closed symbols) rod dispersions. Data were taken from figures 2 and 3. The dashed line corresponds to the situation where tracer dynamics is predicted by the effective dispersion viscosity.

effect of the tracer size. The effective Stokes friction seems to apply for the large tracers, but does not apply for the small ones, which diffuse and sediment considerably faster than expected from the rod viscosity. The different tracer dynamics observed in the two different host dispersions is indeed related to host dynamics: the shorter rods fluctuate on a time scale comparable to a typical (short-time) diffusion time for the tracers, whereas the longer rods form slowly relaxing, entangled structures down to very low densities. These slow (rotational) relaxations manifest themselves also clearly in a high low-shear viscosity (figure 3), a slow birefringence decay [4] and non-ergodicity in the dynamic structure factor [4].

A noteworthy conclusion of figure 4 is also that the friction factor is the same for long-time diffusion and sedimentation, also when this friction clearly deviates from an effective Stokes friction. This confirms that in both techniques mobile tracer silica spheres probe the (static or fluctuating) rod environment over long distances. So the classical ‘Svedberg relation’  $D/s = m/kT$  at infinite dilution for determining the mass of a particle with an unknown friction factor  $f$  is also valid when  $f$  is not the usual Stokes friction.

#### 4. Conclusions

We have investigated long-time self-diffusion of monodisperse fluorescent silica tracer spheres in dispersions of rigid silica rods of known viscosity for various sphere and rod dimensions. These stable sphere–rod mixtures appear to be very suitable for a study of the tracer dynamics, which can be monitored *in situ* using FRAP and sedimentation. Our main findings are that the sphere friction factor, which was always the same for diffusion and sedimentation, is determined only by the macroscopic rod viscosity when the rods are relatively mobile (dilute regime). However, when the host-rod dynamics is slow (semi-dilute regime) the tracer friction is much smaller than expected from the host viscosity, and markedly dependent on the sphere/rod size ratio. From these findings we conclude that the dynamics of tracer spheres in dispersions of host rods markedly depends on the mobility of the host rods. Current theoretical models do not adequately take this effect of host-rod dynamics into account.

### **Acknowledgments**

This work is part of the research programme of the Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for Scientific Research (NWO).

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