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## DIFFUSION OF SPHERES IN SUSPENSION: THREE-BODY HYDRODYNAMIC INTERACTION EFFECTS

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We calculate for a suspension the concentration dependence of the (self-) diffusion coefficient, including terms of second order in the density. These terms contain two- and three-sphere hydrodynamic interaction effects of comparable size

1. The (self-) diffusion coefficient of spherical particles in suspension is concentration dependent, due to direct hard-sphere interactions between the particles and due to a coupling of their motion via the fluid. This coupling is called hydrodynamic interaction. Though properties of suspensions have been studied extensively [1], all theoretical treatments have taken the hydrodynamic couplings to be pairwise additive. This assumption is certainly valid in a dilute suspension, but it was not all clear whether or not three-body hydrodynamic interactions could be neglected at higher densities.

Recently [2] the many-body hydrodynamic interaction problem has been solved in a systematic way. Using the explicit forms of the two- and three-sphere contributions to the mobilities — for a given configuration of the spheres — we will calculate the concentration dependence of the (self-) diffusion coefficient, including second-order density corrections. The importance of three-body hydrodynamic interactions will be evident from our result.

2. Consider  $N$  spheres with radii  $a_i$  and position vectors  $\mathbf{r}_i$  ( $i = 1, 2, \dots, N$ ), moving in an unbounded incompressible fluid with viscosity  $\eta$ , which is otherwise at rest. If we describe the motion of the fluid by the linearized Navier–Stokes equation, we can express the velocity  $\mathbf{u}_i$  of sphere  $i$  and the velocity of the fluid  $\mathbf{v}(\mathbf{r})$  at  $\mathbf{r}$  as a linear combination of the forces  $\mathbf{K}_j$ , exerted by the fluid on each of the spheres  $j$ .

$$\mathbf{u}_i = - \sum_{j=1}^N \boldsymbol{\mu}_{ij} \cdot \mathbf{K}_j, \quad i = 1, 2, \dots, N, \quad (1)$$

$$\mathbf{v}(\mathbf{r}) = - \sum_{j=1}^N \mathbf{S}_j(\mathbf{r}) \cdot \mathbf{K}_j. \quad (2)$$

The mobility tensors  $\boldsymbol{\mu}_{ij}$  and  $\mathbf{S}_j(\mathbf{r})$  depend on the whole configuration of the  $N$  spheres, a term in  $\boldsymbol{\mu}_{ij}$  which depends on the positions of  $s$  spheres is said to reflect  $s$ -body hydrodynamic interactions.

The sphere mobilities  $\boldsymbol{\mu}_{ij}$  are calculated in ref. [2] as a series expansion in the inverse interparticle distance  $1/R$ . Explicit expressions are given up to order  $(1/R)^7$ . Up to this order two-, three- and four-body hydrodynamic interactions contribute. We can derive the fluid mobilities  $\mathbf{S}_j(\mathbf{r})$  from these sphere mobilities by considering an extra sphere with position vector  $\mathbf{r}_{N+1} = \mathbf{r}$  and negligible radius  $a_{N+1}$ .

$$\mathbf{S}_j(\mathbf{r}) = \lim_{a_{N+1} \rightarrow 0} \boldsymbol{\mu}_{N+1,j}, \quad j = 1, 2, \dots, N. \quad (3)$$

3. Consider a homogeneous suspension of  $N$  equal-sized spherical particles (with radius  $a$ ) in a large volume  $V$ . We define average mobilities.

$$\boldsymbol{\mu} = N^{-1} \left\langle \sum_{i=1}^N \sum_{j=1}^N \boldsymbol{\mu}_{ij} \right\rangle, \quad (4)$$

$$\mu_s = N^{-1} \left\langle \sum_{i=1}^N \mu_{ii} \right\rangle, \quad (5)$$

$$S = \left\langle \sum_{j=1}^N S_j(\mathbf{r}) \right\rangle, \quad (6)$$

where  $\langle \rangle$  denotes an average over all the allowed configurations of the  $N$  spheres, with equal weight. (In (6) the average is only over those configurations for which there is a fluid at position  $\mathbf{r}$ .)

The average mobilities are related to the (bulk-) diffusion coefficient  $D$  and the self-diffusion coefficient  $D_s$  by generalized Einstein relations [3,4]:

$$D = (\mu - S) \varphi \partial g / \partial \varphi|_{p, T}, \quad (7)$$

$$D_s = \mu_s kT, \quad (8)$$

where  $\partial g / \partial \varphi|_{p, T}$  denotes the derivative of the chemical potential per particle  $g$  with respect to the partial volume  $\varphi = \frac{4}{3} \pi a^3 N / V$ , at constant temperature  $T$  and pressure  $p$ ; in (8)  $k$  denotes Boltzmann's constant. The short-time self-diffusion coefficient  $D_s$  describes the diffusion of a single particle, over distances small compared to the interparticle separation [5].

4. We have calculated the average mobilities and the diffusion coefficients as a series expansion in the partial volume  $\varphi$ , up to and including terms of order  $\varphi^2$ . To this order we need consider only two- and three-body hydrodynamic interactions. The density expansion of the two- and three-sphere distribution functions is well known [6]. The one-sphere and two-sphere fluid correlation functions can then be found by treating the fluid at  $\mathbf{r}$  as a sphere of negligible radius.

Numerical integration gives <sup>\*1</sup>:

$$\mu - S = I(6\pi\eta a)^{-1} (1 - 5.44\varphi + 8.51\varphi^2 + 8.49\varphi^2), \quad (9)$$

$$\mu_s = I(6\pi\eta a)^{-1} (1 - 1.73\varphi - 0.93\varphi^2 + 1.80\varphi^2). \quad (10)$$

<sup>\*1</sup> Use was made of the adaptive stratified Monte Carlo integration program RIWIAD [7]. Details of the calculations will be published elsewhere.

The first of the two terms of order  $\varphi^2$  is due to two-body hydrodynamic interactions, while the second one results from three-body contributions. Using the result [3]:

$$\varphi \partial g / \partial \varphi|_{p, T} = kT(1 - \varphi)(1 + 8\varphi + 30\varphi^2) \quad (11)$$

one then finds

$$D = I kT(6\pi\eta a)^{-1} (1 + 1.56\varphi + 0.91\varphi^2), \quad (12)$$

$$D_s = I kT(6\pi\eta a)^{-1} (1 - 1.73\varphi + 0.88\varphi^2). \quad (13)$$

The terms of order  $\varphi$  are well known [3,8,9]. If we had considered only two-body hydrodynamic interactions, we would have found for the term of order  $\varphi^2$  in  $D$ :  $-7.58\varphi^2$  and in  $D_s$ :  $-0.93\varphi^2$ . We have here-with confirmed the surmise made in ref. [2] that: "*specific hydrodynamic interaction of three spheres may not a priori be neglected when evaluating the diffusion coefficient of a suspension which is not dilute*". That two-sphere hydrodynamic interactions do not suffice to describe the properties of suspensions at higher densities has recently also been established experimentally, by dynamic light-scattering measurements of  $D_s$  [10].

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