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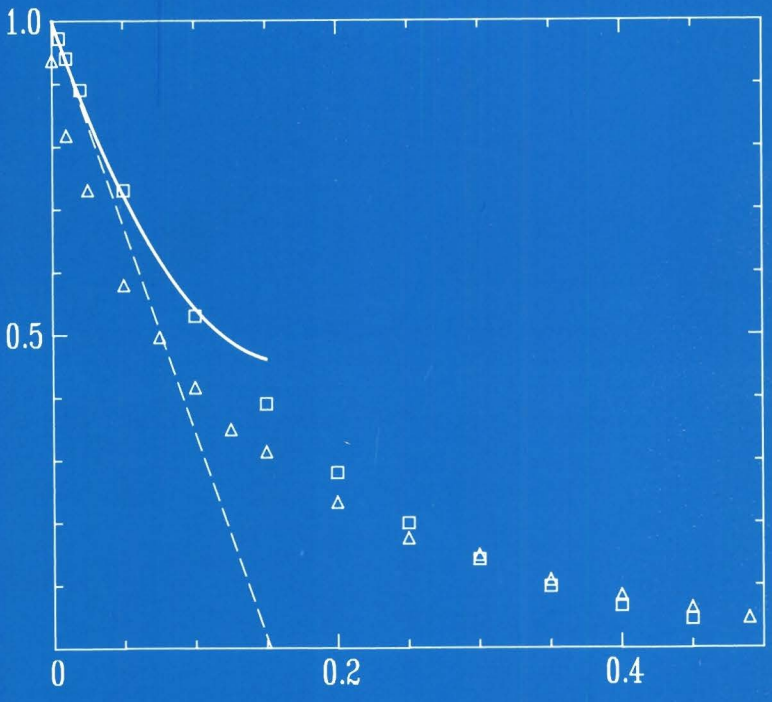

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The Dependence of Transport Coefficients of Suspensions on Quasistatic and Retarded Hydrodynamic Interactions

THE DEPENDENCE OF TRANSPORT COEFFICIENTS OF SUSPENSIONS ON QUASISTATIC AND RETARDED HYDRODYNAMIC INTERACTIONS

proefschrift

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en

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Contents

Chapter 1 INTRODUCTION

1.1 Introduction

In the last few decades more and more theoretical as well as experimental attention has been paid to the hydrodynamic interaction between colloidal particles in a suspension. The growing theoretical interest in this field stems from the fact that the experimental research has been making considerable progress. We refer to the development of the laser, which can be used in light scattering experiments, and the development of the photon correlator. The photon correlator is an important part of the experimental apparatus in a light scattering experiment as it allows the intensity autocorrelation function of scattered laserlight to be calculated. This function is used to determine the position correlation function of the Brownian particles in a suspension. These developments made it possible to compare theoretical results with experimental data. Even theoreticians have made progress with the help of the technical advances of the last decades. We can think of the fast numerical calculations on computers and the development of a new area in computational physics called "Brownian dynamics", i.e. computer simulations with a system of Brownian particles. It is in this context that we have studied the behaviour of transport coefficients of suspensions. In this thesis we describe quasistatic (Stokes limit) and retarded hydrodynamic interactions in suspensions while special attention is paid to the effects of hydrodynamic interactions on transport properties like self–diffusion of the particles, sedimentation and effective viscosity.

For a long time the behaviour of the transport coefficients of suspensions has been an area of intensive research. In the field of experimental research we can think of experiments where the sedimentation velocity of the particles in a dispersion, the effective

viscosity of a suspension as a function of shear rate or the self–diffusion coefficient of a test particle in the suspension etc. are measured. From all these experiments it can be concluded that hydrodynamic interactions between the particles play an important role. These effects are prominent in the case of e.g. sedimentation of neutral colloidal particles. This problem can also be treated theoretically and several authors have presented expressions to describe the effects of hydrodynamic interactions on the sedimentation velocity. It was not an easy task to incorporate hydrodynamic interactions as these interactions are long ranged. Because of this long range character of the hydrodynamic interactions it is not possible to determine configurational averages, which are necessary to obtain statistical averaged values for transport coefficients. Batchelor solved this problem for the sedimentation problem satisfactorily for dilute suspensions and his result is [1]

$$U_s = U_o(1-6.55\varphi)\,, \tag{1.1}$$

with U_s the sedimentation velocity of a particle, U_o its velocity in an infinitely diluted suspension and φ the volume fraction of suspended particles. The order φ contribution is completely determined by including two particle hydrodynamic interactions among the suspended particles only. Batchelor also obtained an expression describing the short time self–diffusion coefficient of particles in a dilute suspension. His famous result is [2]

$$D_s^t = D_o^t(1-1.83\varphi)\,, \tag{1.2}$$

with D_o^t the diffusion coefficient of a particle in an infinitely diluted suspension. The two relations described above look so simple that the theoretical problems associated with their derivations are easily overlooked. In the introductions to the chapters 2 and 3 of this thesis we present a short historical review of the theoretical developments concerning two particle hydrodynamic interactions. It will be obvious that this review cannot be complete.

Apart from the theoretical and experimental investigations a new area of research has been developed with the general name computational physics. Part of this area deals with the simulation of systems of particles. Two distinct methods are available and have been widely used. The first, the Monte Carlo method, was developed in the early fifties by Metropolis et al. [3], the other some years later by Alder and Wainwright and called the molecular dynamics method [4]. With these simulation techniques the properties of e.g. atomic and molecular liquids can be studied. These methods can, in principle, also be used for hard sphere dispersions with hydrodynamic interactions among the particles. Brady and Bossis developed an approximate method to perform this kind of simulations and called it Stokesian dynamics simulation [5]. With this method, which is related to the non–equilibrium molecular dynamics method, phenomena like ordering effects and shear thinning and thickening can be studied, as well as transport coefficients like diffusion, sedimentation and viscosity of suspensions. The results of Stokesian dynamics simulation are supplementary to the experimental results although they have some attractive advantages compared to experiments, because the parameters of the suspension can be controlled much better. One can think of e.g. the monodispersity of the particles in the suspension.

In this thesis we present a method to study both quasistatic and retarded hydrodynamic interactions between spherical particles in an unbounded fluid. We start with a method to determine the mobility matrix of an N–particle cluster of hydrodynamically interacting spheres. In the past several methods to obtain the mobility matrix were presented e.g. by Mazur and van Saarloos [6] and Felderhof et al. [7] for the N particle problem and by Jeffrey and Onishi [8] for the two particle problem. Why a new method? There is much to say in favour of it. In the first place we want to have a method to our disposal that can give us expressions of the components of the grand mobility matrix which are not power expansions in typical inverse interparticle distances as is the case in the reflection method. The convergence behaviour of these single power expansions is not

very good for small interparticle distances. In the two particle case this disadvantage is not really important but in the three particle case it is not easy to evaluate the terms of the single power expansion, so convergence difficulties cannot be overcome in this way. Another important reason for developing this method deals with its extension including retardation effects: i.e. hydrodynamic interactions take time to propagate and do not act instantaneously as assumed in the Stokes approximation. Using this approach hydrodynamic interactions at finite frequencies ω are considered and series expansions for the components of the mobility matrix for the low frequency range are obtained only [9]. Therefore it is necessary to express these components as a function of the interparticle distance R and frequency ω in another way. In this thesis we present a method to determine the mobility matrix for a system of two particles immersed in an unbounded fluid described by the time dependent incompressible linearized Navier–Stokes equation in chapter 7 and use the results to calculate the correlation functions of Brownian particles. Finally we want to point out that our method has the advantage that we can obtain relatively easily numerical results for the mobility matrix of three and more particle clusters and some transport coefficients. This is possible as the N–particle problem can be reduced to a set of linear equations.

1.2 Thesis overview

In chapter 2 we describe the method to solve the problem of N particles, interacting hydrodynamically, in an unbounded fluid with an externally imposed flow. The results of this method, in the case of the two particle problem, are presented in chapter 3. Many results are already known and this enables us to test the convergence behaviour of our method. We also present some new results. An alternative approach to the calculation of the effective viscosity of a hard sphere suspension as function of volume fraction φ follows

in chapter 4. This approach is based on ideas produced by Saito. In chapter 5 we present the results of a study of the three particle cluster in an unbounded fluid. Virial expansions of some transport coefficients, including three particle effects, are described there. Chapter 6 deals with the problem of one particle in an externally imposed flow. The fluid motion is described by the time dependent incompressible linearized Navier–Stokes equations. We present the results of a study on retarded hydrodynamic interactions between two spherical particles in chapter 7 and will end this thesis with a short conclusion.

Most of the work reflected in the chapters 2,3 and 7 has been published [10,11]. The work conveyed in the chapters 4,5 and 6 has been or will be submitted for publication, although in a slightly different form.

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Chapter 2 THEORY OF QUASISTATIC HYDRODYNAMIC INTERACTIONS AMONG SPHERICAL PARTICLES

2.1 Introduction

Theoretical research on the hydrodynamic interaction among spherical particles immersed in an unbounded fluid started already at the beginning of this century when Smoluchowski treated this problem with the method of reflections [1]. The many particle problem is extremely complex. In the past much attention was already paid to the two particle problem. In the twenties Stimson and Jeffery solved the problem of the hydrodynamic interaction between two spherical particles, each with a velocity parallel to their line of centers, in a bipolar coordinate system [2]. One of the later efforts was the calculation of the components of the grand resistance matrix (or the grand mobility matrix) of a two particle system [3] as an expansion in powers of a/R, with a the particle radius and R the interparticle distance. Some researchers like Burgers [4], Batchelor [5] and Felderhof [6] treated the two particle problem in this way. In the case of dilute colloidal suspensions it is sufficient to take into account the two particle interactions only and it is possible to use the above mentioned results for the calculation of the transport coefficients. Since the hydrodynamic interactions between particles in a suspension are long ranged, one should extrapolate these results to more concentrated suspensions with caution. In recent years many attempts have been made to calculate the many particle hydrodynamic interactions in suspensions. Mazur and van Saarloos have developed a method to calculate the components of the mobility matrix taking these interactions into account [7]. Their method is based on the induced force formalism.

We present in this chapter a method to solve the many particle problem using the

time independent incompressible linearized Navier–Stokes equations (in the following abbreviated by N.S. equations) and the boundary conditions on the surfaces of the spherical particles. This study lines up with earlier studies of Felderhof et al. because we use their formalism of basic functions to describe the fluid velocity fields. There are several reasons to develop this method for the calculation of the components of the mobility matrix (or friction matrix) for the many particle problem, as already outlined in chapter 1. One of the reasons is the fact that we are able to calculate these components to a desired accuracy by simply solving a set of linear equations. It is not difficult to show that this method gives expressions for the components of the mobility matrix which are not expansions in powers of a/R, as is the case by use of the method of reflections, but in a fraction where we can take down both the numerator and the denominator as expansions in powers of a/R. In case of the two particle problem this kind of expansions, obtained by the presented method, has the disadvantage that we are not able to use the results for analytical calculations like e.g. the determination of configurationally averaged quantities such as short time self–diffusion coefficients but this disadvantage is not important for the three and more particle problem. In that case the configurationally averaged quantities should be calculated numerically anyway. We are able to compare the expressions for the components of the mobility matrix for the two particle problem, resulting from this method, with those obtained by the reflection method calculated by Schmitz and Felderhof [8] and by Jones and Schmitz [9]. From this comparison we can conclude that, in general, this method leads to a faster and more systematic convergence when the two spherical particles approach each other, than the single expansion of the method of reflections does. We expect that this effect is even more important in the case of three and more particle interactions. The reason for this behaviour is the simultaneous calculation of the effects of the perturbations of the fluid velocity field, caused by the presence of the translating and rotating particles, on the components of the grand mobility matrix in contrast to the reflection method where this calculation is performed successively. In that case it is very difficult to obtain single

expansions for the components of the mobility matrix so the results of the method presented in this paper should be reliable. We study this reliability for two particle interactions in chapter 3 by comparing our results with those obtained from the reflection method. Apart from this comparison we present in that chapter some new results too.

2.2 The formulation of the N–particle problem

We consider a system of N spherical particles with radii a_i, i = 1,2,..,N, immersed in an incompressible, unbounded fluid with an incoming fluid velocity field $\underline{v}_o(\underline{r})$. For the moment we assume that $\underline{v}_o(\underline{r})$ is arbitrary but satisfies the incompressible, linearized Navier–Stokes equations. The particles have velocities $\underline{U}_i$ and rotational velocities $\underline{\Omega}_i$. Their centres have position vectors $\underline{R}_i$ with respect to the origin O. The particles are of such small size that the Reynolds number of the fluid motion induced by the particles is small, Re<<1. With this assumption we can neglect the non–linear term in the Navier–Stokes equation. The equations of motion for the fluid, the N.S. equations, have the following form:

$$\eta_o \nabla^2 \underline{v}(\underline{r}) - \nabla p(\underline{r}) = 0 \,, \tag{2.1}$$

$$\nabla \cdot \underline{v}(\underline{r}) = 0 \,. \tag{2.2}$$

Here $\underline{v}(\underline{r})$ is the fluid velocity, $p(\underline{r})$ is the pressure and η_o is the shear viscosity. We suppose stick boundary conditions at the surface S_i of particle i,

$$\underline{v}(\underline{r}) = \underline{U}_i + \underline{\Omega}_i \times (\underline{r} - \underline{R}_i) \,, \quad \text{with } \underline{r} \epsilon S_i, \; i \epsilon \{1,..,N\} \,. \tag{2.3}$$

To preserve linearity we treat the position vector $\underline{R}_i$ as independent of the time t. This

linearization is equivalent to omitting a term of order $(\underline{U}_i \cdot \nabla)\underline{v}(\underline{r})$ in the N.S. equations, which is justified because of the smallness of the Reynolds number. The smallness of Re implies that the characteristic time of particle displacement is much larger than the viscous time a^2/ν, with ν the kinematic viscosity of the fluid. There is some literature on this point e.g. in an article of Hauge and Martin–Lof [10] and the remarks in a review article of Herczynski and Pienkowska [11]. After calculation of $\underline{v}(\underline{r})$ and $p(\underline{r})$ we are able to determine the pressure tensor $\Pi(\underline{r})=p(\underline{r})I-2\eta_o(\nabla\underline{v}(\underline{r}))^s$. The pressure tensor can be used to determine the force $\underline{F}_i$, the torque $\underline{T}_i$ and the stresslet S_i, exerted by the fluid on particle i. The force $\underline{F}_i$ is defined as

$$\underline{F}_i = -\int_{S_i} \Pi(\underline{r}_i)\cdot d\underline{S}\,, \tag{2.4}$$

with $d\underline{S}$ an infinitesimal element of surface pointing into the fluid. For a spherical particle with radius a_i,

$$\underline{F}_i = -a^2 \int_{|\underline{r}_i|=a_i} \underline{\Pi}_r(\underline{r}_i)d\Omega_i\,, \tag{2.5}$$

with $d\Omega_i$ the element of solid angle with respect to the center of particle i and

$$\underline{\Pi}_r(\underline{r}) \equiv \Pi(\underline{r})\cdot\hat{e}_r = p(\underline{r})\hat{e}_r - \eta_o\left[\frac{\partial}{\partial r} - \frac{1}{r}\right]\underline{v}(\underline{r}) - \frac{\eta_o}{r}\nabla(\underline{r}\cdot\underline{v}(\underline{r}))\,. \tag{2.6}$$

The vector $\hat{e}_r$ is the radial unit vector in a spherical coordinate system. In the same way one can obtain an expression of the torque $\underline{T}_i$ exerted by the fluid on particle i. The definition of the torque is

$$\underline{T}_i = -\int_{S_i} (\underline{r}_i \times \Pi(\underline{r}_i))\cdot d\underline{S}\,. \tag{2.7}$$

For a spherical particle,

$$\underline{T}_i = -a^3 \int_{|\underline{r}_i|=a_i} (\hat{e}_r \times \underline{\Pi}_r(\underline{r}_i)) d\Omega_i \,. \tag{2.8}$$

The stresslet $\mathbf{S}_i$ is the symmetric and traceless part of the first moment of the force distribution integrated over the surface of particle i. In the case of spherical particles we have the following expression:

$$\mathbf{S}_i = -a^3 \int_{|\underline{r}_i|=a_i} \overline{\hat{e}_r \Pi(\underline{r}_i) \cdot \hat{e}_r}\, d\Omega_i \,, \tag{2.9}$$

where $\overline{\hat{e}_r \Pi(\underline{r}) \cdot \hat{e}_r}$ is the traceless and symmetric part of $\hat{e}_r \Pi(\underline{r}) \cdot \hat{e}_r$:

$$\overline{\hat{e}_r \Pi(\underline{r}) \cdot \hat{e}_r} = \tfrac{1}{2}(\hat{e}_r \underline{\Pi}_r(\underline{r}) + \underline{\Pi}_r(\underline{r}) \hat{e}_r) - \tfrac{1}{3}\mathbf{I}(\underline{\Pi}_r(\underline{r}) \cdot \hat{e}_r) \,. \tag{2.10}$$

We are especially interested in the grand mobility matrix, the analogue of the grand resistance matrix defined by Happel and Brenner [3]. This mobility matrix relates the velocity difference between the particle and the surface averaged incoming fluid velocity field with the forces, torques and stresslets, exerted by the fluid on the particles, etc. This relation is expressed, with the shorthand notations $\underline{U}=(\underline{U}_1,\ldots,\underline{U}_N)$, $\underline{U}_o=(\underline{U}_{o1},\ldots,\underline{U}_{oN})$ etc., by the following equation:

$$\begin{bmatrix} \underline{U}-\underline{U}_o \\ \underline{\Omega}-\underline{\Omega}_o \\ -\mathbf{G}_o \end{bmatrix} = -\begin{bmatrix} \mu^{tt} & \mu^{tr} & \mu^{td} \\ \mu^{rt} & \mu^{rr} & \mu^{rd} \\ \mu^{dt} & \mu^{dr} & \mu^{dd} \end{bmatrix} \cdot \begin{bmatrix} \underline{F} \\ \underline{T} \\ \mathbf{S} \end{bmatrix} , \tag{2.11}$$

where $\underline{U}_o$, $\underline{\Omega}_o$ and $\mathbf{G}_o$ are the incoming fluid velocity, vorticity and rate of strain, respectively, averaged over the surface of the respective particles. It is important to note that this relation differs from the one introduced by Schmitz and Felderhof [8], their grand mobility matrix is a partially inverted grand resistance matrix. The μ^{tt} etc. are matrices with

$$\mu^{tt} = \begin{bmatrix} \mu^{tt}_{11} \cdot\cdot \mu^{tt}_{1N} \\ \vdots \quad\quad \vdots \\ \mu^{tt}_{N1} \cdot\cdot \mu^{tt}_{NN} \end{bmatrix}, \tag{2.12}$$

where μ^{tt}_{ij} is a mobility tensor. The upper indices t, r and d refer to "translational", "rotational" and "dipole" respectively. The dot in eq. (2.11) stands for a contraction of tensors. It should be emphasized that in this notation for the mobility tensors no distinction has been made between tensors of different rank (an exception is made for vectors, of course). In eq. (2.11) e.g. the matrix μ^{tt} consists of second rank tensors and the matrix μ^{dd} consists of fourth rank tensors. Finally we want to point out the following symmetry relations for the components of the mobility matrix, which have the same form as those presented by Schmitz and Felderhof [8]:

$$\mu^{tt}_{ij,\alpha\beta} = \mu^{tt}_{ji,\beta\alpha}, \quad \mu^{tr}_{ij,\alpha\beta} = \mu^{rt}_{ji,\beta\alpha}, \quad \mu^{td}_{ij,\alpha\beta\gamma} = -\mu^{dt}_{ji,\beta\gamma\alpha}, \tag{2.13}$$

$$\mu^{rr}_{ij,\alpha\beta} = \mu^{rr}_{ji,\beta\alpha}, \quad \mu^{rd}_{ij,\alpha\beta\gamma} = -\mu^{dr}_{ji,\beta\gamma\alpha}, \quad \mu^{dd}_{ij,\alpha\beta\gamma\delta} = \mu^{dd}_{ji,\gamma\delta\alpha\beta}.$$

Our aim is the determination of the grand mobility matrix (eq. (2.11)).

2.3 The set of basic solutions

We present a complete set of basic solutions of the N.S. equations which is convenient for our problem of spherical particles in an unbounded fluid. The idea is not new. Lamb presented a set of basic solutions convenient for this kind of problems in his book [12]. We follow here an elegant method of Schmitz and Felderhof [13]. Before presenting their set of basic solutions we introduce the vector spherical harmonics $\underline{A}_{lm}(\theta,\varphi)$, $\underline{B}_{lm}(\theta,\varphi)$ and $\underline{C}_{lm}(\theta,\varphi)$, used by Schmitz and Felderhof in their formulation of

the basic solutions. The vector spherical harmonics are defined in the following way:

$$\text{(2.14a)} \qquad \underline{A}_{lm}(\theta,\varphi) \equiv lY_{lm}(\theta,\varphi)\hat{e}_r + \frac{\partial Y_{lm}(\theta,\varphi)}{\partial\theta}\hat{e}_\theta + \frac{1}{\sin\theta}\frac{\partial Y_{lm}(\theta,\varphi)}{\partial\varphi}\hat{e}_\varphi ,$$

$$\text{(2.14b)} \qquad \underline{B}_{lm}(\theta,\varphi) \equiv \underline{A}_{lm}(\theta,\varphi) - (2l+1)Y_{lm}(\theta,\varphi)\hat{e}_r ,$$

$$\text{(2.14c)} \qquad \underline{C}_{lm}(\theta,\varphi) \equiv \frac{1}{\sin\theta}\frac{\partial Y_{lm}(\theta,\varphi)}{\partial\varphi}\hat{e}_\theta - \frac{\partial Y_{lm}(\theta,\varphi)}{\partial\theta}\hat{e}_\varphi = \underline{A}_{lm}(\theta,\varphi)\times\hat{e}_r .$$

$Y_{lm}(\theta,\varphi)$ are the spherical harmonics and $\hat{e}_r$, $\hat{e}_\theta$ and $\hat{e}_\varphi$ are the unit vectors in a spherical coordinate system. The vector functions $\underline{A}_{lm}(\theta,\varphi)$, $\underline{B}_{lm}(\theta,\varphi)$ and $\underline{C}_{lm}(\theta,\varphi)$ are related to the vector spherical harmonics $\underline{Y}_{jlm}(\theta,\varphi)$ defined by Edmonds [14]. The relations are

$$\text{(2.15a)} \qquad \underline{A}_{lm}(\theta,\varphi) = \sqrt{l(2l+1)}\,\underline{Y}_{l,l-1,m}(\theta,\varphi) ,$$

$$\text{(2.15b)} \qquad \underline{B}_{lm}(\theta,\varphi) = \sqrt{(l+1)(2l+1)}\,\underline{Y}_{l,l+1,m}(\theta,\varphi) ,$$

$$\text{(2.15c)} \qquad \underline{C}_{lm}(\theta,\varphi) = -i\sqrt{l(l+1)}\,\underline{Y}_{l,l,m}(\theta,\varphi) ,$$

with i the imaginary unit. These vector spherical harmonics constitute a complete orthonormal set of vector functions on the unit sphere:

$$\text{(2.16)} \qquad \int \underline{Y}_{jlm}(\theta,\varphi)\cdot\underline{Y}^*_{pqr}(\theta,\varphi)\mathrm{d}\Omega = \delta_{jp}\delta_{lq}\delta_{mr} ,$$

with δ_{jp} etc. the Kronecker symbols. With this inner product we obtain the following orthogonality relations for our vector spherical harmonics $\underline{A}_{lm}(\theta,\varphi)$, $\underline{B}_{lm}(\theta,\varphi)$ and $\underline{C}_{lm}(\theta,\varphi)$:

$$\text{(2.17a)} \qquad \int \underline{A}_{lm}(\theta,\varphi)\cdot\underline{A}^*_{pq}(\theta,\varphi)\mathrm{d}\Omega = l(2l+1)\delta_{lp}\delta_{mq} ,$$

$$\text{(2.17b)} \qquad \int \underline{B}_{lm}(\theta,\varphi)\cdot\underline{B}^*_{pq}(\theta,\varphi)\mathrm{d}\Omega = (l+1)(2l+1)\delta_{lp}\delta_{mq} ,$$

(2.17c) $$\int \underline{C}_{lm}(\theta,\varphi)\cdot\underline{C}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = l(l+1)\delta_{lp}\delta_{mq} .$$

Inner products of $\underline{A}_{lm}(\theta,\varphi)$ with $\underline{B}^{*}_{pq}(\theta,\varphi)$ etc. are zero. To conclude we present a simple relation between the vector functions $\underline{A}_{lm}(\theta,\varphi)$ and $\underline{B}_{lm}(\theta,\varphi)$ on the one hand and the solid spherical harmonics $\phi^{+}_{lm}(\underline{r})$ and $\phi^{-}_{lm}(\underline{r})$ on the other, where

(2.18) $$\phi^{+}_{lm}(\underline{r}) = r^{l}Y_{lm}(\theta,\varphi) , \qquad \phi^{-}_{lm}(\underline{r}) = r^{-(l+1)}Y_{lm}(\theta,\varphi) .$$

The relations are

(2.19) $$\underline{A}_{lm}(\theta,\varphi) = r^{-(l-1)}\nabla\phi^{+}_{lm}(\underline{r}) , \qquad \underline{B}_{lm}(\theta,\varphi) = r^{l+2}\nabla\phi^{-}_{lm}(\underline{r}) .$$

We are now able to present the basic solutions, introduced by Schmitz and Felderhof, with respect to a coordinate system with origin O. The basic solutions that behave regularly for $|\underline{r}|\to\infty$, are

(2.20a) $$\underline{v}_{lm\alpha}(\underline{r}) = \frac{l}{(l+1)(2l+1)} r^{-(l+2)}\underline{B}_{lm}(\theta,\varphi) ,$$

(2.20b) $$\underline{v}_{lm\beta}(\underline{r}) = \frac{1}{l(l+1)} r^{-(l+1)}\underline{C}_{lm}(\theta,\varphi) ,$$

(2.20c) $$\underline{v}_{lm\gamma}(\underline{r}) = \frac{1}{(2l+1)} r^{-l}\left[(l+1)\underline{A}_{lm}(\theta,\varphi) - \frac{l(2l-1)}{2}\underline{B}_{lm}(\theta,\varphi)\right] .$$

For these outgoing basic functions the indices l and m are restricted to $l\geq 1$ and $|m|\leq l$. The accompanying solutions for the pressure are

(2.21) $$p_{lm\alpha}(\underline{r}) = 0 , \quad p_{lm\beta}(\underline{r}) = 0 , \quad p_{lm\gamma}(\underline{r}) = \eta_{o}l(2l-1)r^{-(l+1)}Y_{lm}(\theta,\varphi) .$$

This complete set of basic solutions has been chosen in such way that for all $l \geq 1$, $|m| \leq l$ and $\sigma \in \{\alpha,\beta,\gamma\}$ we have

$$\eta_o \nabla^2 \underline{v}_{lm\sigma}(\underline{r}) - \nabla p_{lm\sigma}(\underline{r}) = 0 \,, \quad \nabla \cdot \underline{v}_{lm\sigma}(\underline{r}) = 0 \,. \tag{2.22}$$

The incoming fluid velocity field should be expanded in terms of an alternative set of basic solutions, which have been introduced by Schmitz and Felderhof also [13]. These basic solutions behave regularly for $|\underline{r}| \to 0$, and have the following form:

$$\underline{w}_{lm\alpha}(\underline{r}) = r^{l-1} \underline{A}_{lm}(\theta,\varphi) \,, \tag{2.23a}$$

$$\underline{w}_{lm\beta}(\underline{r}) = r^{l} \underline{C}_{lm}(\theta,\varphi) \,, \tag{2.23b}$$

$$\underline{w}_{lm\gamma}(\underline{r}) = r^{l+1} \left[\frac{(l+1)(2l+3)}{2l} \underline{A}_{lm}(\theta,\varphi) + \underline{B}_{lm}(\theta,\varphi) \right] . \tag{2.23c}$$

For the pressure we have

$$p^{inc}_{lm\alpha}(\underline{r}) = 0 \,, \quad p^{inc}_{lm\beta}(\underline{r}) = 0 \,, \quad p^{inc}_{lm\gamma}(\underline{r}) = \eta_o \frac{(l+1)(2l+1)(2l+3)}{l} r^l Y_{lm}(\theta,\varphi) \,. \tag{2.24}$$

For these incoming basic functions the indices l and m are again restricted to $l \geq 1$ and $|m| \leq l$. It is evident that this set of basic solutions satisfies the N.S. equations for each l, m and $\sigma \in \{\alpha,\beta,\gamma\}$ separately as is the case with the outgoing basic functions (see eq. (2.22)).

Consider a system of N spherical particles in an unbounded fluid, with an externally imposed flow, at the positions $\underline{R}_1,..,\underline{R}_N$ and an arbitrary point $\underline{r}$ in that fluid. The fluid velocity at the point $\underline{r}$ in the fluid is not governed by the external flow only, because the N particles have velocities $\underline{U}_i$ and angular velocities $\underline{\Omega}_i$ which will influence the fluid velocity at that point. The velocity field $\underline{v}(\underline{r})$ is a solution of the N.S. equations, a set of linear

differential equations and for that reason we can write the total velocity field as a sum of N velocity fields $\underline{v}_i(\underline{r}_i)$, each separately satisfying the N.S. equations, and the incoming flow field $\underline{v}_o(\underline{r})$, or alternatively:

$$\underline{v}(\underline{r})-\underline{v}_o(\underline{r}) = \sum_{i=1}^{N} \underline{v}_i(\underline{r}_i) , \quad \text{with: } \underline{r}_i = \underline{r}-\underline{R}_i . \tag{2.25}$$

The vector $\underline{r}_i$ is the position vector of the point $\underline{r}$ with respect to the origin O_i, the centre of particle i. All the N velocity fields of the r.h.s. of eq. (2.25) can be expressed in terms of outgoing basic solutions (eqs. (2.20a)–(2.20c)) and for every velocity field $\underline{v}_i(\underline{r}_i)$ we have a set of coefficients: $\{\alpha^i_{lm}, \beta^i_{lm}, \gamma^i_{lm}\}$. Similarly we can express the incoming flow field in terms of the incoming basic functions (eqs. (2.23a)–(2.23c)), and introduce the set of expansion coefficients $\{\alpha^o_{lm}, \beta^o_{lm}, \gamma^o_{lm}\}$. The resulting expression for the total fluid velocity $\underline{v}^i(\underline{r}_i) = \underline{v}(\underline{r}_i+\underline{R}_i)$, which is the fluid velocity defined with respect to the origin O_i, is

$$\begin{aligned} \underline{v}^i(\underline{r}_i) - \sum_{\substack{l\geq 1 \\ m}} \Big[& \alpha^o_{lm}\underline{w}_{lm\alpha}(\underline{r}_i+\underline{R}_i) + \beta^o_{lm}\underline{w}_{lm\beta}(\underline{r}_i+\underline{R}_i) + \gamma^o_{lm}\underline{w}_{lm\gamma}(\underline{r}_i+\underline{R}_i)\Big] \\ = \sum_{\substack{l\geq 1 \\ m}} \Big[& \alpha^i_{lm}\underline{v}_{lm\alpha}(\underline{r}_i) + \beta^i_{lm}\underline{v}_{lm\beta}(\underline{r}_i) + \gamma^i_{lm}\underline{v}_{lm\gamma}(\underline{r}_i)\Big] \\ + \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\substack{l\geq 1 \\ m}} \Big[& \alpha^j_{lm}\underline{v}_{lm\alpha}(\underline{r}_i+\underline{R}_{ij}) + \beta^j_{lm}\underline{v}_{lm\beta}(\underline{r}_i+\underline{R}_{ij}) + \gamma^j_{lm}\underline{v}_{lm\gamma}(\underline{r}_i+\underline{R}_{ij})\Big] , \end{aligned} \tag{2.26}$$

where $\underline{R}_{ij} = \underline{R}_i-\underline{R}_j$ is the position vector of the center of particle i with respect to the center of particle j. In an analogous way we have for the pressure field $p^i(\underline{r}_i)$

$$p^i(\underline{r}_i) - \sum_{\substack{l\geq 1 \\ m}} \gamma^o_{lm} p^{inc}_{lm\gamma}(\underline{r}_i+\underline{R}_i) = \sum_{\substack{l\geq 1 \\ m}} \gamma^i_{lm} p_{lm\gamma}(\underline{r}_i) + \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\substack{l\geq 1 \\ m}} \gamma^j_{lm} p_{lm\gamma}(\underline{r}_i+\underline{R}_{ij}) . \tag{2.27}$$

2.4 Calculation of the mobility matrix

The velocity field $(\underline{v}(\underline{r})-\underline{v}_o(\underline{r}))$ is a sum of the N velocity fields $\underline{v}_i(\underline{r}_i)$. These velocity fields can be decomposed with the help of the set of basic solutions defined in section 2.3. If we want to calculate the coefficients α^i_{lm}, β^i_{lm} and γ^i_{lm} for i = 1,..,N then it is necessary to evaluate the following inner products:

$$(2.28) \qquad \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i ,$$

$$(2.29) \qquad \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i ,$$

$$(2.30) \qquad \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i ,$$

with

$$(2.31) \qquad \underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i) = \underline{v}_i(\underline{r}_i) + \sum_{\substack{j=1 \\ j\neq i}}^{N} \underline{v}_j(\underline{r}_i+\underline{R}_{ij}) .$$

We want to calculate these inner products for all i = 1,..,N, $p \geq 1$ and $|q| \leq p$. This kind of inner products is easy to evaluate for the first part of the r.h.s. of eq. (2.31) but difficult for the second part. This has to do with the fact that the velocity fields $\underline{v}_j(\underline{r}_i+\underline{R}_{ij})$, for j≠i, are decomposed in basic solutions which are defined with respect to the origin O_j instead of the origin O_i. We can rewrite these velocity fields, with the help of the general form of the Hobson formula, in terms of vector functions defined with respect to the origin O_i. The general form of the Hobson formula expressing a solid spherical harmonic $\phi^-_{lm}(\underline{r}_j)$, defined with respect to O_j, in terms of the solid spherical harmonics $\phi^+_{lm}(\underline{r}_i)$, has, according to de

Wette and Nijboer [15], the following form:

$$\phi^{-}_{lm}(\underline{r}_j) = \sum_{\substack{s\geq 0\\ t}} \frac{n_{st}}{(s+t)!} M^{ji}_{lm;st}(\underline{R}_{ij})\phi^{+}_{st}(\underline{r}_i)\,, \quad |\underline{r}_i| < R_{ij} \tag{2.32}$$

with

$$M^{ji}_{lm;st}(\underline{R}_{ij}) = (-1)^{s+t}\frac{(l+s-m+t)!}{n_{lm}(l-m)!}\, n_{l+s,m-t}\frac{Y_{l+s,m-t}(\xi_{ij},\eta_{ij})}{R^{l+s+1}_{ij}}, \tag{2.33}$$

$$n_{lm} = \left[\frac{4\pi}{(2l+1)}\frac{(l+m)!}{(l-m)!}\right]^{\frac{1}{2}} \tag{2.34}$$

and $\underline{R}_{ij}=(R_{ij},\xi_{ij},\eta_{ij})$, the vector pointing from O_j to O_i. Note that $\underline{R}_{ji}=(R_{ij},\pi-\xi_{ij},\eta_{ij}+\pi)$. We see that $M^{ji}_{lm;st}(\underline{R}_{ij})=0$ if $|m-t|>l+s$. After substitution of the general form of the Hobson formula into the equation for the velocity field $\underline{v}^i(\underline{r}_i)$ we obtain for that velocity field

$$\begin{aligned}\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i) = \sum_{\substack{l\geq 1\\ m}} r_i^{-l}\Bigg[&\frac{l}{(l+1)(2l+1)}\,\alpha^i_{lm} r_i^{-2}\underline{B}_{lm}(\theta_i,\varphi_i)\\ &+\frac{1}{l(l+1)}\beta^i_{lm} r_i^{-1}\underline{C}_{lm}(\theta_i,\varphi_i)+\frac{1}{(2l+1)}\gamma^i_{lm}\Big[(l+1)\underline{A}_{lm}(\theta_i,\varphi_i)-\frac{l(2l-1)}{2}\underline{B}_{lm}(\theta_i,\varphi_i)\Big]\\ &+\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{\substack{s\geq 0\\ t}}\frac{n_{st}}{(s+t)!}\, r_i^{s-1}\Bigg[\frac{l}{(l+1)(2l+1)}\,\alpha^j_{lm}\underline{A}_{st}(\theta_i,\varphi_i)M^{ji}_{lm;st}\\ &+\frac{1}{l(l+1)}\beta^j_{lm}\Big[r_i\underline{C}_{st}(\theta_i,\varphi_i)-(\underline{R}_{ij}\times\underline{A}_{st}(\theta_i,\varphi_i))\Big]M^{ji}_{lm;st}\\ &+(l+1)\gamma^j_{lm}\Big[r_i(\underline{r}_i+\underline{R}_{ij})Y_{st}(\theta_i,\varphi_i)-\frac{(l-2)}{2(l+1)}(\underline{r}_i+\underline{R}_{ij})^2\underline{A}_{st}(\theta_i,\varphi_i)\Big]M^{ji}_{lm;st}\Bigg]\Bigg]\,.\end{aligned} \tag{2.35}$$

Schmitz and Felderhof derived this kind of expressions of these basic solutions appropriate for the two particle case [16].

We can calculate the inner products (eqs. (2.28)–(2.30)) by substituting first the r.h.s. of eq. (2.35) for $\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i)$ in these inner products. Next we can express them in the translational and angular velocities of the particles by means of the boundary conditions. Combination of both results give us an infinite set of linear equations which we shall use to calculate the components of the grand mobility matrix. We shall start with the more difficult task, the direct calculation of the inner products with the help of the r.h.s. of eq. (2.35) for $\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i)$, $i\in\{1,..,N\}$. We do not give full details in this section but refer the interested reader to appendix I. There we have collected all the items necessary to obtain these inner products, such as special integrals and products of spherical harmonics. The final results are

$$
\begin{aligned}
(2.36)\qquad & \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{A}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i = p(p+1)a_i^{-p}\gamma^i_{pq} \\
& + \frac{n_{pq}}{(p+q)!}\,a_i^{p-1}\sum_{\substack{j=1\\ j\neq i}}^{N}\Bigg[p(2p+1)\sum_{\substack{l\geq 1\\ m}}\frac{l}{l(l+1)(2l+1)}\,\alpha^j_{lm}M^{ji}_{lm;pq} \\
& - i(2p+1)\sum_{\substack{l\geq 1\\ m}}\frac{(lq+mp)}{l(l+1)}\,\beta^j_{lm}M^{ji}_{lm;p-1,q} + \tfrac{1}{2}pa_i^2\sum_{\substack{l\geq 1\\ m}} l(2l-1)\gamma^j_{lm}M^{ji}_{lm;pq} \\
& - \tfrac{1}{2}p(2p+1)\sum_{\substack{l\geq 1\\ m}}\frac{l(2l-1)}{(2l+2p-1)}R_{ij}^2\gamma^j_{lm}M^{ji}_{lm;pq} + \frac{(2p+1)}{(2p-1)}\sum_{\substack{l\geq 1\\ m}}\frac{(2l+2p-lp-1)}{(2l+2p-1)} \\
& \times((lq+mp)(2(lq+mp)-(m+q))-(lp+mq)(l+p-1))\gamma^j_{lm}M^{ji}_{lm;p-2,q}\Bigg],
\end{aligned}
$$

$$
\begin{aligned}
(2.37)\qquad & \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{B}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i = pa_i^{-(p+2)}\alpha^i_{pq} \\
& - \tfrac{1}{2}p(p+1)(2p-1)a_i^{-p}\gamma^i_{pq} + \frac{n_{pq}}{(p+q)!}\,\frac{p}{(2p+3)}\,a_i^{p+1}\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{\substack{l\geq 1\\ m}} l(2l-1)\gamma^j_{lm}M^{ji}_{lm;pq},
\end{aligned}
$$

$$(2.38)\qquad \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot \underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = a_i^{-(p+1)}\beta^i_{pq}$$

$$-\frac{n_{pq}}{(p+q)!}a_i^p \sum_{\substack{j=1\\ j\neq i}}^{N}\left[p\sum_{\substack{l\geq 1\\ m}}\frac{1}{(l+1)}\beta^j_{lm}M^{ji}_{lm;pq} + i\sum_{\substack{l\geq 1\\ m}}(lq+mp)(2l-1)\gamma^j_{lm}M^{ji}_{lm;p-1,q}\right].$$

In this thesis we shall present the results of studies of two special kinds of incoming flow fields. The first one is trivial because we assume that the fluid is at rest at infinity. This case can be studied by putting $\underline{v}_o(\underline{r})=\underline{0}$ in all the equations derived above and below. In the second case the flow field has the form:

$$(2.39)\qquad \underline{v}_o(\underline{r}) = G_o\cdot\underline{r}\,.$$

In this equation for the incident flow, G_o represents a constant rate of strain tensor. If we define the incoming fluid velocity field with respect to the origin of particle i we obtain

$$(2.40)\qquad \underline{v}_o(\underline{r}_i+\underline{R}_i) = G_o\cdot\underline{r}_i + G_o\cdot\underline{R}_i \equiv \underline{v}_o(\underline{r}_i) + \underline{U}_{oi}\,,$$

with $\underline{U}_{oi}$ the incoming flow at the center of particle i or equivalently the incoming fluid velocity field averaged over the surface of particle i (see in this context eq. (2.11)). We can expand $\underline{v}_o(\underline{r}_i)$ in terms of basic solutions (eqs. (2.23a)–(2.23c)). There are few coefficients which are nonzero. These are the coefficients related to the linear basic functions, i.e. $\alpha^o_{2m}\neq 0$, with $|m|\leq 2$, and $\beta^o_{1m}\neq 0$, $|m|\leq 1$. We can rewrite eq. (2.40) in the following way:

$$(2.41)\qquad \underline{v}_o(\underline{r}_i+\underline{R}_i) = \sum_{m=-2}^{+2}\alpha^o_{2m}\underline{w}_{2m\alpha}(\underline{r}_i) + \sum_{m=-1}^{+1}\beta^o_{1m}\underline{w}_{1m\beta}(\underline{r}_i) + \underline{U}_{oi}\,.$$

We can now calculate the inner products (eqs. (2.28)–(2.30)) with the help of the boundary conditions as defined in section 2.2 (eq. (2.3)). These boundary conditions can be

rewritten with respect to the new origin O_i:

$$\underline{v}^i(\underline{r}_i) = \underline{U}_i + \underline{\Omega}_i \times \underline{r}_i \quad \text{for } |\underline{r}_i| = a_i \text{ and } i \in \{1,..,N\} . \tag{2.42}$$

Further we use eq. (2.41) which is determined using boundary conditions at infinity concerning the external flow. The first inner product (eq. (2.28)) now becomes

$$\begin{aligned} &\int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i) - \underline{v}_o(\underline{r}_i+\underline{R}_i)) \cdot \underline{A}^*_{pq}(\theta_i,\varphi_i) d\Omega_i \\ &\qquad = (\underline{U}_i - \underline{U}_{io}) \cdot \int_{|\underline{r}_i|=a_i} \underline{A}^*_{pq}(\theta_i,\varphi_i) d\Omega_i - a_i(\underline{\Omega}_i - \underline{\Omega}_{io}) \cdot \int_{|\underline{r}_i|=a_i} \underline{C}^*_{pq}(\theta_i,\varphi_i) d\Omega_i , \end{aligned} \tag{2.43}$$

where $\underline{U}_{io}$ and $\underline{\Omega}_{io}$ are the surface averaged incoming fluid velocity and vorticity respectively. In this relation we have used the following vector equality: $\underline{A}^*_{pq} \cdot (\underline{\Omega}_i \times \underline{r}_i) = r_i \underline{\Omega}_i \cdot (\hat{e}_r \times \underline{A}^*_{pq})$. It is obvious that these relations are valid for all $i \in \{1,..,N\}$. The integrals with the vector spherical harmonics can be calculated in a straightforward way and we find

$$\begin{aligned} &\int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i) - \underline{v}_o(\underline{r}_i+\underline{R}_i)) \cdot \underline{A}^*_{pq}(\theta_i,\varphi_i) d\Omega_i = \tfrac{3}{2}\delta_{p,1} \Big[n_{11}(\delta_{q,-1} - \delta_{q,1})(U_{ix} - U_{oix}) \\ &\qquad + in_{11}(\delta_{q,-1} + \delta_{q,1})(U_{iy} - U_{oiy}) + 2n_{10}\delta_{q,0}(U_{iz} - U_{oiz}) \Big] - 10a_i \alpha^o_{2q} \delta_{p,2} , \end{aligned} \tag{2.44}$$

$$\int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i) - \underline{v}_o(\underline{r}_i+\underline{R}_i)) \cdot \underline{B}^*_{pq}(\theta_i,\varphi_i) d\Omega_i = 0 , \tag{2.45}$$

$$\int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i) - \underline{v}_o(\underline{r}_i+\underline{R}_i)) \cdot \underline{C}^*_{pq}(\theta_i,\varphi_i) d\Omega_i \tag{2.46}$$

$$= a_i \delta_{p,1}\left[n_{11}(\delta_{q,-1}-\delta_{q,1})\Omega_{ix}+in_{11}(\delta_{q,-1}+\delta_{q,1})\Omega_{iy}+2n_{10}\delta_{q,0}\Omega_{iz}\right]-2a_i\beta^o_{1q}\delta_{p,1}\,.$$

The constants n_{10} and n_{11} are special cases of n_{lm} (eq. (2.34)). The last inner product can be rewritten by using the surface averaged vorticity,

$$(2.47)\qquad \underline{\Omega}_{oi} = \frac{1}{4\pi}\int_{|\underline{r}_i|=a_i} \tfrac{1}{2}(\nabla\times\underline{v}_o(\underline{r}_i+\underline{R}_i))d\Omega_i$$
$$= \frac{3}{8\pi}\left[n_{11}(\beta^o_{1,-1}-\beta^o_{1,1})\hat{e}_x - in_{11}(\beta^o_{1,-1}+\beta^o_{1,1})\hat{e}_y + 2n_{10}\beta^o_{1,0}\hat{e}_z\right] \equiv \underline{\Omega}_o\,,$$

with $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$ the unit vectors in a Cartesian coordinate system. This expression is independent of the chosen origin. Combination of eqs. (2.46) and (2.47) gives

$$(2.48)\qquad \int_{|\underline{r}_i|=a_i} (\underline{v}^i(\underline{r}_i)-\underline{v}_o(\underline{r}_i+\underline{R}_i))\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i$$
$$= a_i\delta_{p,1}\left[n_{11}(\delta_{q,-1}-\delta_{q,1})(\Omega_{ix}-\Omega_{ox})+in_{11}(\delta_{q,-1}+\delta_{q,1})(\Omega_{iy}-\Omega_{oy})+2n_{10}\delta_{q,0}(\Omega_{iz}-\Omega_{oz})\right].$$

Combining eqs. (2.36), (2.37) and (2.38) with eqs. (2.44), (2.45) and (2.48) respectively we obtain an infinite set of linear equations of the coefficients $\{\alpha^i_{lm},\beta^i_{lm},\gamma^i_{lm}\}$ with $i\in\{1,\ldots,N\}$. It is possible to solve this set of linear equations if we define an upper limit for the allowed values of l and p, e.g. $l_{max}=p_{max}=L$. With this restriction we say that all the coefficients α^i_{lm}, β^i_{lm} and γ^i_{lm} are zero for $l>L$. In the simplest case we take $L=1$ and as a consequence of this decision the indices m and q can take the values -1, 0 and 1 only. We have now a set of 9N linear equations from which we can calculate the 9N coefficients α^i_{1m}, β^i_{1m} and γ^i_{1m}. We call this solution a first order solution of our set of linear equations. With the upper limit L we obtain $3L(L+2)N$ linear equations with the same number of unknown coefficients and we can calculate the so called L^{th} order solution of the set of linear

equations. The decision, which upper limit L we want to use, depends on some factors e.g. the desired numerical accuracy of the coefficients α^i_{lm} etc. and the convergence behaviour with increasing L of the coefficients which we are interested in. We come to this point later on.

With the help of this formulation it is not difficult to derive from eqs. (2.26) and (2.27) a relation between the force $\underline{F}_i$, torque $\underline{T}_i$ and stresslet $\mathbf{S}_i$, exerted by the fluid on particle i, on one hand and some of the expansion coefficients on the other hand. That is the aim of the next section.

2.5 Force, torque and stresslet as function of the coefficients

We start this section with the derivation of expressions of the force $\underline{F}_i$ and torque $\underline{T}_i$, exerted by the fluid on particle i, in terms of some coefficients. These derivations are relatively simple. Such a derivation for the stresslet $\mathbf{S}_i$ requires much more space. We give a short outline of how this result can be achieved. The derivation for the two particle case is presented in appendix II. It can be skipped, without consequences for the understanding of the sequel, if one is interested in the final result only.

The relation between the force $\underline{F}_i$ and torque $\underline{T}_i$ on the one hand and the coefficients $\{\alpha^i_{lm},\beta^i_{lm},\gamma^i_{lm}\}$ on the other hand can be determined with the help of the eqs. (2.5), (2.6), (2.8), (2.26) and (2.27). In the first place one can calculate the total pressure tensor Π^i, which is defined in the following way:

$$\Pi^i(\underline{r}_i) = \Pi_o(\underline{r}_i+\underline{R}_i) + \Pi_i(\underline{r}_i) + \sum_{\substack{j=1\\ j\neq i}}^{N} \Pi_j(\underline{r}_i+\underline{R}_{ij}) \,. \tag{2.49}$$

This definition is equivalent with the definitions of $\underline{v}^i(\underline{r}_i)$ and $p^i(\underline{r}_i)$. The equation of the force $\underline{F}_i$ is

$$\underline{F}_i = -\int_{S_i} \Pi_o(\underline{r}_i+\underline{R}_i)\cdot d\underline{S}_i - \int_{S_i} \Pi_i(\underline{r}_i)\cdot d\underline{S}_i - \sum_{\substack{j=1\\ j\neq i}}^{N} \int_{S_i} \Pi_j(\underline{r}_i+\underline{R}_{ij})\cdot d\underline{S}_i \,. \tag{2.50}$$

The solutions (2.26) and (2.27) can be considered to exist also within the particles. Then the pressure tensor $\Pi_i(\underline{r}_i)$ has a singularity within the surface of particle i and no singularities outside the volume of particle i, for all i = 1,..,N. The pressure tensor belonging to the incoming fluid velocity field has also no singularities within the surfaces of the particles. Thus the pressure tensors $\Pi_o(\underline{r}_i+\underline{R}_i)$ and $\Pi_j(\underline{r}_i+\underline{R}_{ij})$ have no singularities within the surface S_i and by using Gauss' theorem we can rewrite eq. (2.50). The result is

$$\underline{F}_i = -\int_{S_i} \Pi_i(\underline{r}_i)\cdot d\underline{S}_i - \int_{V_i} \nabla_i\cdot\left[\Pi_o(\underline{r}_i+\underline{R}_i)+\sum_{\substack{j=1\\ j\neq i}}^{N} \Pi_j(\underline{r}_i+\underline{R}_{ij})\right] dV_i \,, \tag{2.51}$$

where V_i is the volume within the surface of particle i. An alternative formulation of the N.S. eq. (2.1) is: $\nabla\cdot\Pi(\underline{r}) = 0$, which is also valid for the constituents of the pressure tensor because of the linearity of the N.S. equations. If $\underline{R}_{ij}$ is a constant then $\nabla_i=\nabla_j$. The last term of eq. (2.51) disappears. Using eqs. (2.5) and (2.6) gives

$$\underline{F}_i = a_i^2\left[-\int p_i(\underline{r}_i)\hat{e}_r d\Omega_i + \eta_o\left[\frac{\partial}{\partial r_i}-\frac{1}{r_i}\right]\int \underline{v}_i(\underline{r}_i)d\Omega_i + \frac{\eta_o}{r_i}\int \nabla_i\left[\underline{r}_i\cdot\underline{v}_i(\underline{r}_i)\right]d\Omega_i\right]\Bigg|_{r_i\downarrow a_i} . \tag{2.52}$$

After a straightforward calculation of the integrals we obtain

$$\underline{F}_i = -\tfrac{8}{2}\eta_o\left[n_{11}\left[\gamma^i_{1,-1}-\gamma^i_{1,1}\right]\hat{e}_x - in_{11}\left[\gamma^i_{1,-1}+\gamma^i_{1,1}\right]\hat{e}_y + 2n_{10}\gamma^i_{1,0}\hat{e}_z\right] . \tag{2.53}$$

The $\hat{e}_x$, $\hat{e}_y$ and $\hat{e}_z$ are the unit vectors in a Cartesian coordinate system. We can obtain an expression for the torque $\underline{T}_i$ exerted by the fluid on particle i in an analogous way:

$$\underline{T}_i = \eta_o a_i^3 \left[\left[\frac{\partial}{\partial r_i} - \frac{1}{r_i} \right] \left[\hat{e}_r \times \underline{v}_i(\underline{r}_i) d\Omega_i + \frac{1}{r_i} \left[\hat{e}_r \times \nabla \left[\underline{r}_i \cdot \underline{v}_i(\underline{r}_i) \right] d\Omega_i \right] \right] \right|_{r_i \downarrow a_i}$$

$$= -\tfrac{3}{2}\eta_o \left[n_{11} \left[\beta^i_{1,-1} - \beta^i_{1,1} \right] \hat{e}_x - i n_{11} \left[\beta^i_{1,-1} + \beta^i_{1,1} \right] \hat{e}_y + 2 n_{10} \beta^i_{1,0} \hat{e}_z \right] . \tag{2.54}$$

The expressions for the force $\underline{F}_i$ and the torque $\underline{T}_i$ are valid for all values of i=1,..,N and we see that, for each particle, they depend each on three coefficients only.

In the same way one is able to express the stresslet S_i, exerted by the fluid on particle i, in terms of some coefficients, in this case the γ^i_{2m}. The final expression is

$$S_i = -\tfrac{3}{2}\eta_o \sum_{m=-2}^{+2} \gamma^i_{2m} \sigma_{2m} , \tag{2.55}$$

with

$$\sigma_{2,0} = -\frac{8\pi}{3 n_{20}} (I - 3\hat{e}_z \hat{e}_z) , \tag{2.56a}$$

$$\sigma_{2,1} = -\frac{8\pi}{n_{21}} \left[(\hat{e}_x \hat{e}_z + \hat{e}_z \hat{e}_x) + i(\hat{e}_y \hat{e}_z + \hat{e}_z \hat{e}_y) \right] = -\sigma^*_{2,-1} , \tag{2.56b}$$

$$\sigma_{2,2} = \frac{16\pi}{n_{22}} \left[(\hat{e}_x \hat{e}_x - \hat{e}_y \hat{e}_y) + i(\hat{e}_x \hat{e}_y + \hat{e}_y \hat{e}_x) \right] = \sigma^*_{2,-2} . \tag{2.56c}$$

There are N+1 sources contributing to S_i, the incoming fluid velocity $\underline{v}_o(\underline{r})$, which gives the stresslet S^0_i, and the N velocity fields $\underline{v}_j(\underline{r}_j)$ scattered from the particles, which give the contributions S^j_i. We first determine the contribution of the incoming flow field. The result is

$$S^0_i = \eta_o a^3 \sum_{m=-2}^{+2} \alpha^o_{2m} \sigma_{2m} . \tag{2.57}$$

In an analogous way, using the expansion in basic solutions of $p_i(\underline{r}_i)$ and $\underline{v}_i(\underline{r}_i)$, we obtain:

$$S_i^i = -\tfrac{9}{10}\eta_o \sum_{m=-2}^{+2} \gamma_{2m}^i \sigma_{2m} . \tag{2.58}$$

The determination of S_i^j, with $j \neq i$, requires more extensive calculations. First we have to express the pressure $p_j(\underline{r}_j)$ and the fluid velocity $\underline{v}_j(\underline{r}_j)$ in terms of $\underline{r}_i$ (see eqs. (2.26) and (2.27)). The final result has the following form:

$$\sum_{\substack{j=1 \\ j\neq i}}^{N} S_i^j = -\eta_o a^3 \sum_{q=-2}^{+2} \alpha_{2q}^o \sigma_{2q} - \tfrac{3}{5}\eta_o \sum_{q=-2}^{+2} \gamma_{2q}^i \sigma_{2q} = -S_i^0 + \tfrac{2}{3}S_i^i . \tag{2.59}$$

The final form for the stresslet S_i, exerted by the fluid on particle i, is now

$$S_i = S_i^0 + S_i^i + \sum_{\substack{j=1 \\ j\neq i}}^{N} S_i^j = -\tfrac{3}{2}\eta_o \sum_{q=-2}^{+2} \gamma_{2q}^i \sigma_{2q} = \tfrac{5}{3}S_i^i . \tag{2.60}$$

It may be noted that in the limit $R \to \infty$ all the S_i^j should be zero if $j \neq i$, so that eqs. (2.59) and (2.60) lead to

$$\lim_{R\to\infty} S_i = \tfrac{5}{2}S_i^0 , \tag{2.61}$$

where the coefficient $\frac{5}{2}$ corresponds to the Einstein coefficient in the virial expansion of the effective viscosity of hard sphere suspensions.

2.6 Conclusion

The main part of this chapter concerns a method for the determination of the grand mobility matrix for a system of N spherical particles, interacting hydrodynamically, with stick boundary conditions in an unbounded fluid with an externally imposed flow. We conclude that we are able to derive the grand mobility matrix from a set of linear equations

(eqs. (2.36)–(2.38)). In general, this can be done with the help of a computer programme for solving linear equations. In the next chapter we present the results of a comparison of the convergence behaviour of our method with the results obtained from the reflection method in the case of the two particle problem which was already intensively studied in the past. The aim of this comparison is not especially to show the superiority of our method concerning the two particle problem, because this is in the two particle problem not very relevant. The shown convergence behaviour is important if we study three particle hydrodynamic interactions because not many results are available to compare our results with, so it is necessary to have an idea about the convergence behaviour. Furthermore we shall study the reliability of this method by calculating some transport coefficients and comparing them with results from the literature. Finally we want to remark that the same procedure is followed in studying retarded hydrodynamic interactions in suspensions. The results are presented in chapter 7.

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Chapter 3 THE TWO PARTICLE PROBLEM, A COMPARISON AND SOME NEW RESULTS

3.1 Introduction

We now consider a suspension where the concentration of the suspended particles is very small. The volume fraction $\varphi = \frac{4}{3}\pi a^3 n_o << 1$, where a is the radius of the particles and n_o is the concentration of suspended particles. Under this circumstance the best approach to the problem is to consider two particle hydrodynamic interactions only. Furthermore we assume that the fluid is at rest at infinity, viz. $\underline{v}_o(\underline{r})=\underline{0}$. We can calculate the effects of the two particle hydrodynamic interaction on the components of the grand mobility matrix using the method presented in chapter 2. Some of the results are already known with great accuracy. We refer to the work of Jeffrey and Onishi (expansion in powers of a/R) [1], Kim and Mifflin (numerical calculations via a boundary collocation technique) [2], Ladd (numerical calculations using the induced force formalism) [3,4] and, of course, the work of Cichocki, Felderhof, Jones and Schmitz [5–8]. These authors express the components of the grand mobility matrix as an expansion in powers of a/R. In this section we can compare some of their results with the results obtained in chapter 2 and discuss the convergence behaviour of the components of the grand mobility matrix. This gives an indication of the reliability of our results and the usefulness of this method. This is important if we want to apply our method in the study of three particle hydrodynamic interactions. We further focus special attention on the first order virial coefficients of the short time translational and rotational self–diffusion coefficients D_s^t and D_s^r. On the other hand we present some new results such as the second order virial coefficient of D_s^r and the virial expansion, to second order in φ, of the rotational counterpart of the sedimentation velocity, Ω_s. We

compare these results with computer simulation results of hard sphere suspensions.

3.2 The set of linear equations for the two particle problem

In the case of dilute suspensions we can modify the set of linear equations (eqs. (2.36)–(2.38), (2.44), (2.45) and (2.48)). First we set N=2, $a_1=a_2=a$ and $R_{12}=R_{21}=R$. Then we put $\underline{v}_o(\underline{r})=\underline{0}$ because we assume that there is no incoming fluid velocity field. We can now choose the two particle centers to be situated on the z–axis of a Cartesian coordinate system. This configuration leads to a considerable simplification of the general form of the Hobson formula (eq. (2.33)) resulting in the formula derived by Hobson [9]. In our notation this formula comes to

$$\phi^-_{lm}(\underline{r}_j) = \sum_{\substack{s\geq 0\\ t}} \frac{n_{st}}{(s+t)!}\, M^{ji}_{lm;st}(R)\phi^+_{st}(\underline{r}_i)\,, \quad |\underline{r}_i|<R \text{ and } i,j\in\{1,2\}\,, \tag{3.1}$$

$$M^{21}_{lm;st}(R) = (-1)^{s+t}\,\frac{(l+s)!}{n_{lm}(l-t)!}\,R^{-(l+s+1)}\delta_{m,t}\,, \tag{3.2}$$

$$M^{12}_{lm;st}(R) = (-1)^{l+s}\,M^{21}_{lm;st}(R)\,. \tag{3.3}$$

The presence of the Kronecker symbol in the Hobson formula results in a decoupling of the set of linear equations for different values of the azimuthal indices (m and q). Finally we introduce the new set of coefficients $\{A^i_{lm},B^i_{lm},C^i_{lm}\}$, appropriate for the two particle case, which have the following relation with the previously introduced set of coefficients:

$$\alpha^1_{lm} = (-1)^{l+m}\,n_{lm}R^{l+2}A^1_{lm}\,, \qquad \alpha^2_{lm} = n_{lm}R^{l+2}A^2_{lm}\,, \tag{3.4}$$

$$\beta^1_{lm} = i(-1)^{l+m}\, n_{lm} R^{l+1} B^1_{lm}\,, \qquad \beta^2_{lm} = -i n_{lm} R^{l+1} B^2_{lm}\,, \tag{3.5}$$

$$\gamma^1_{lm} = (-1)^{l+m}\, n_{lm} a R^{l-1} C^1_{lm}\,, \qquad \gamma^2_{lm} = n_{lm} a R^{l-1} C^2_{lm}\,, \tag{3.6}$$

The analogue of the eqs. (2.36)–(2.38) for the two particle problem is

$$\frac{\Delta_i^1\, x^{p-1}}{p(p+1)n_{pq}} \int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i)\cdot \underline{A}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i = C^i_{pq} + \frac{(2p+1)}{(p+1)} x^{2p-2} \sum_{l\geq 1} \frac{l}{l(l+1)(2l+1)} \begin{bmatrix} l+p \\ l-q \end{bmatrix} A^j_{lq}$$

$$+ \frac{q(2p+1)}{p(p+1)} x^{2p-2} \sum_{l\geq 1} \frac{1}{l(l+1)} \begin{bmatrix} l+p \\ l-q \end{bmatrix} B^j_{lq} + \frac{1}{2(p+1)} x^{2p+1} \sum_{l\geq 1} l(2l-1) \begin{bmatrix} l+p \\ l-q \end{bmatrix} C^j_{lq}$$

$$- \frac{(2p+1)}{p(p+1)(2p-1)} x^{2p-1} \sum_{l\geq 1} \left[lp(lp-\tfrac{1}{2}(l+p)+1) + q^2(lp-2(l+p)+1) \right] \frac{1}{(l+p)} \begin{bmatrix} l+p \\ l-q \end{bmatrix} C^j_{lq}\,, \tag{3.7}$$

$$A^i_{pq} = \tfrac{1}{2}(p+1)(2p-1)x^3 C^i_{pq} - \frac{1}{(2p+3)} x^{2p+4} \sum_{l\geq 1} l(2l-1) \begin{bmatrix} l+p \\ l-q \end{bmatrix} C^j_{lq}\,, \tag{3.8}$$

where we used also eq. (2.45) and

$$\frac{-i\Delta_i^2\, x^{p+1}}{n_{pq}} \int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i)\cdot \underline{C}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i = B^i_{pq} + p x^{2p+1} \sum_{l\geq 1} \frac{1}{l(l+1)} \begin{bmatrix} l+p \\ l-q \end{bmatrix} B^j_{lq}$$

$$+ q x^{2p+2} \sum_{l\geq 1} (2l-1) \begin{bmatrix} l+p \\ l-q \end{bmatrix} C^j_{lq}\,, \tag{3.9}$$

where $x = \frac{a}{R}$, the ratio of the particle radius a and the interparticle distance R. This ratio is always less than or equal to $\frac{1}{2}$. Furthermore:

$$\Delta^1_i = \begin{cases} (-1)^{p+q} & i=1 \\ 1 & i=2 \end{cases} \quad ; \quad \Delta^2_i = \begin{cases} (-1)^{p+q} & i=1 \\ -1 & i=2 \end{cases} \quad ; \quad \begin{bmatrix} l+p \\ l-q \end{bmatrix} = \frac{(l+p)!}{(l-q)!\,(p+q)!}$$

Finally: if i=1 then j=2 and vice versa. Combination of the eqs. (3.7)–(3.9) with the eqs. (2.44), (2.45) and (2.48) gives the set of linear equations which is necessary for the calculation of the components of the grand mobility matrix.

3.3 The two particle mobility matrix

In this section we pay some attention to the components of the grand mobility matrix. We shall focus on the translational and rotational part of the mobility matrix only, so we are interested in the following relation (see eq. (2.11)):

$$\begin{bmatrix} \underline{U} \\ \underline{\Omega} \end{bmatrix} = -\begin{bmatrix} \mu^{tt} & \mu^{tr} \\ \mu^{rt} & \mu^{rr} \end{bmatrix} \cdot \begin{bmatrix} \underline{F} \\ \underline{T} \end{bmatrix} . \tag{3.10}$$

where $\underline{U}=(\underline{U}_1,\underline{U}_2)$ etc. For small values of the upper limit L we can calculate the components of the grand mobility matrix as a function of x directly and for large values of L it is possible to perform the same calculations with the help of so called algebraic computer programmes like REDUCE. In the case of large values of L we restrict ourselves to numerical calculations of the components of the grand mobility matrix. We have made a programme for the numerical evaluation of these components, which, in principle, is nothing but solving a set of linear equations. This computer programme is obtainable from the author upon request. The calculations consist of the following steps. With the help of the set of linear equations with upper limit L, we first express all the coefficients A^i_{pq}, with $p \geq 1$, B^i_{pq}, with $p \geq 2$, and C^i_{pq}, with $p \geq 2$, for both i=1 and i=2 in terms of the coefficients B^1_{1m}, B^2_{1m}, C^1_{1m} and C^2_{1m} with $m \in \{1,0,-1\}$. In this way we have reduced the set of $6L(L+2)$

linear equations to a set of 12 linear equations. With the help of eqs. (2.53), (2.54), (3.5) and (3.6) we express the coefficients B^i_{1m} and C^i_{1m}, for $m\epsilon\{1,0,-1\}$ and $i\epsilon\{1,2\}$, in terms of the forces $\underline{F}_i$ and torques $\underline{T}_i$ exerted by the fluid on the two particles and substitute the result in the set of linear equations. It is not difficult to see that we can extract the components of the grand mobility matrix from this just created form of the set of linear equations. The calculations can be simplified with the symmetry relations of the components of the grand mobility matrix (see eq. (2.13)) and the fact that for our two particle system, where the particles have the same radius, the components of the grand mobility matrix do not change if the particle labels are interchanged. For the present two particle problem we can write the grand mobility matrix in the following way:

$$(3.11)\qquad \begin{bmatrix} \underline{U}_x \\ \underline{\Omega}_y \\ \underline{U}_y \\ \underline{\Omega}_x \\ \underline{U}_z \\ \underline{\Omega}_z \end{bmatrix} = - \begin{bmatrix} \mu^{tt}_{xx} & \mu^{tr}_{xy} & 0 & 0 & 0 & 0 \\ \mu^{rt}_{yx} & \mu^{rr}_{yy} & 0 & 0 & 0 & 0 \\ 0 & 0 & \mu^{tt}_{xx} & -\mu^{tr}_{xy} & 0 & 0 \\ 0 & 0 & -\mu^{rt}_{yx} & \mu^{rr}_{yy} & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu^{tt}_{zz} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu^{rr}_{zz} \end{bmatrix} \cdot \begin{bmatrix} \underline{F}_x \\ \underline{T}_y \\ \underline{F}_y \\ \underline{T}_x \\ \underline{F}_z \\ \underline{T}_z \end{bmatrix} .$$

In the case $L=2$ we give the results of the calculation of the matrix μ^{tt}_{zz}:

$$(3.12)\qquad \mu^{tt}_{11,zz} = \mu^{tt}_{22,zz} = \frac{-1}{6\pi\eta_o a}\Big[(1-\tfrac{1}{5}x^6-\tfrac{9}{35}x^8) - \Big[(\tfrac{15}{4}x^4 - 12x^6 + \tfrac{48}{5}x^8 + \tfrac{15}{4}x^{12} - \tfrac{117}{5}x^{14} + \tfrac{72}{7}x^{16} + \tfrac{8496}{245}x^{18} - \tfrac{9}{5}x^{22} - \tfrac{72}{7}x^{24} - \tfrac{4752}{245}x^{26} - \tfrac{20736}{1715}x^{28})/ (1 - 25x^6 + 114x^8 - \tfrac{1104}{7}x^{10} + 9x^{16} + \tfrac{288}{7}x^{18} + \tfrac{2304}{49}x^{20})\Big]\Big] ,$$

$$(3.13)\qquad \mu^{tt}_{12,zz} = \mu^{tt}_{21,zz} = \frac{-1}{6\pi\eta_o a}\Big[(\tfrac{3}{2}x - x^3) + \Big[(\tfrac{75}{4}x^7 - 102x^9 + \tfrac{6732}{35}x^{11} - \tfrac{864}{7}x^{13} - 6x^{17} - \tfrac{648}{35}x^{19} + \tfrac{1584}{245}x^{21} + \tfrac{1728}{49}x^{23})/ (1 - 25x^6 + 114x^8 - \tfrac{1104}{7}x^{10} + 9x^{16} + \tfrac{288}{7}x^{18} + \tfrac{2304}{49}x^{20})\Big]\Big] .$$

We can express $\mu^{tt}_{11,zz}$ and $\mu^{tt}_{12,zz}$ in a Taylor expansion around x=0 and the resulting

expressions resemble the results of the reflection method (see e.g. ref.[7]) but in the case that $x \to \frac{1}{2}$ then the denominator differs to much from unity so that we have convergence problems. For that reason we cannot cut off the Taylor expansion very quickly. We meet with this kind of problems in the other components of the grand mobility matrix too.

We want to compare the convergence of our results with the convergence of the results of Schmitz and Felderhof [7] who derived the components of the grand mobility matrix as an expansion in powers of x=a/R. For the comparison we use the following criterion: we expand our L^{th} order expressions around x=0 in a Taylor expansion and compare the coefficients of this Taylor expansion with those derived by Schmitz and Felderhof. Suppose our L^{th} order Taylor expansion for e.g. $\mu^{tt}_{11,zz}(x)$ looks like

$$\mu^{tt}_{11,zz}(x) = \sum_{p=0}^{N} a_p x^p , \quad x<<1 , \tag{3.14}$$

the M^{th} order Taylor expansion of Schmitz and Felderhof looks like

$$\mu^{tt}_{11,zz}(x) = \sum_{p=0}^{M} b_p x^p \tag{3.15}$$

and $a_p = b_p$ for p=1,..,n and $a_{n+1} \neq b_{n+1}$. It is clear that we can choose N and M arbitrarily, so we choose N>n and M>n. Then we compare our L^{th} order result for $\mu^{tt}_{11,zz}(x)$ with the n^{th} order Taylor expansion of Schmitz and Felderhof. We do this for some values of L for all the ten independent components of the grand mobility matrix. In fig. 1 we have plotted the components of the grand mobility matrix as a function of the order L for two values of x=a/R and compare them with the results of Schmitz and Felderhof. We come to the conclusion that the results presented in this chapter are reliable and we see further that these results converge more systematicly if x=0.4 and for some components of the grand mobility matrix even for x=0.5. In fig. 1 we have plotted results of our method up to L=20 in order to compare these results with those obtained from the reflection method. To study the limiting values of the components of the mobility matrix in the case of (nearly) touching spheres higher order results can be taken into account, with L up to 150. In principle we can show the same kind of figures for 0.4<x<0.5 and the

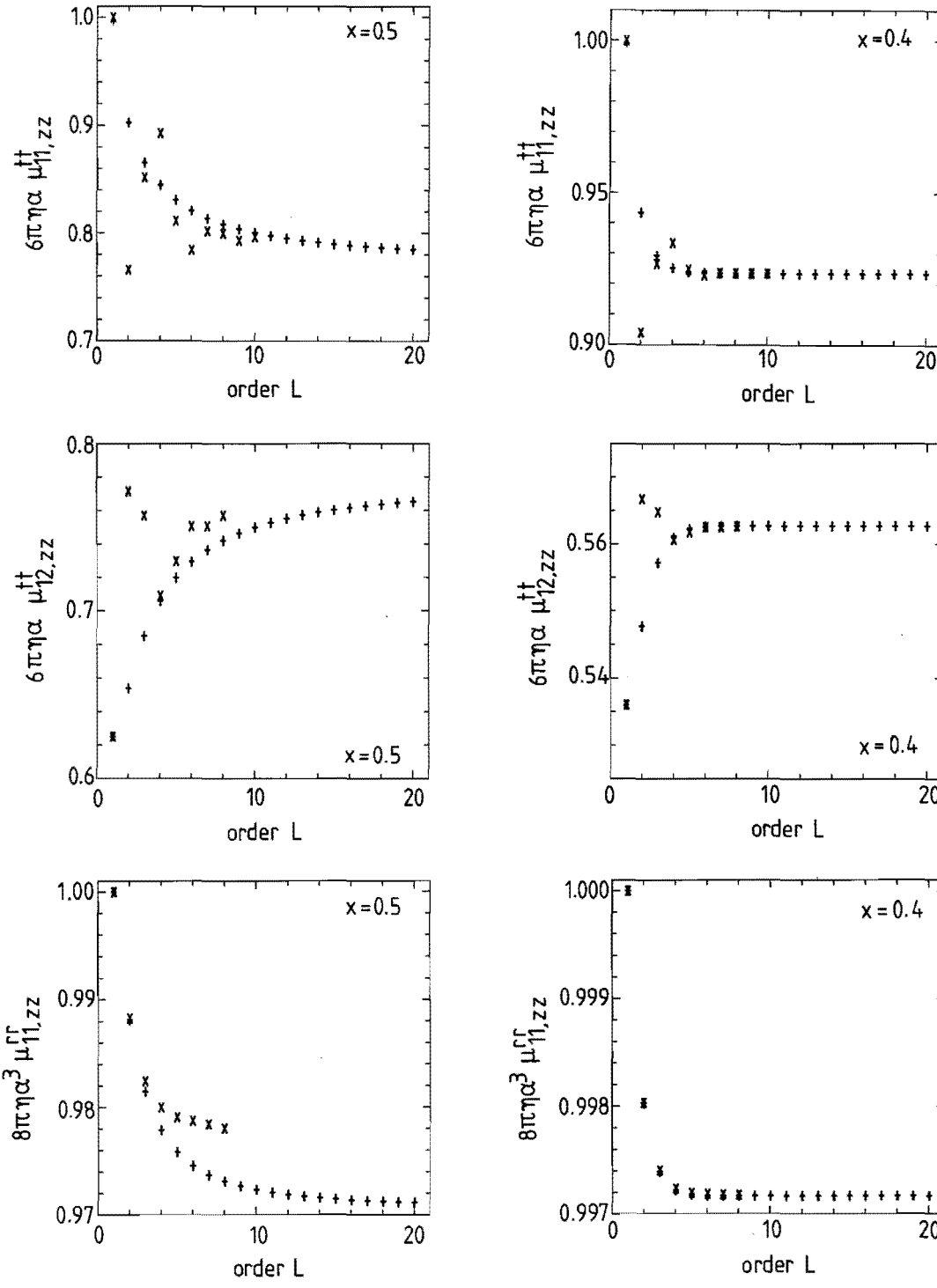
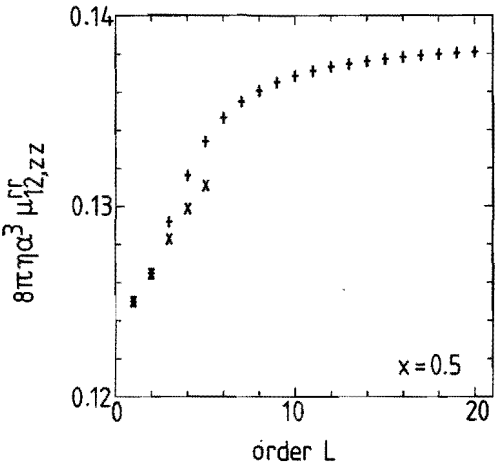
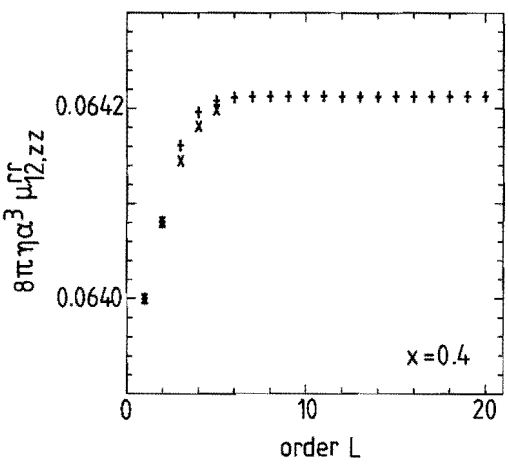
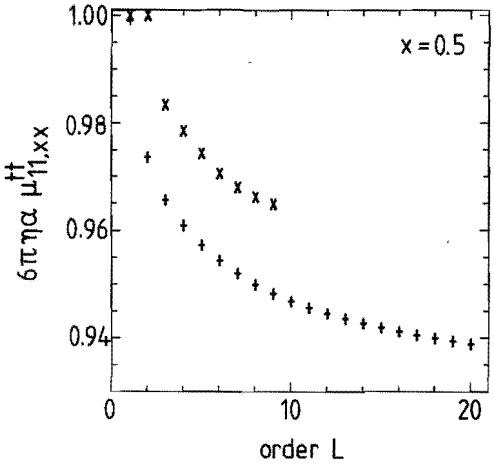
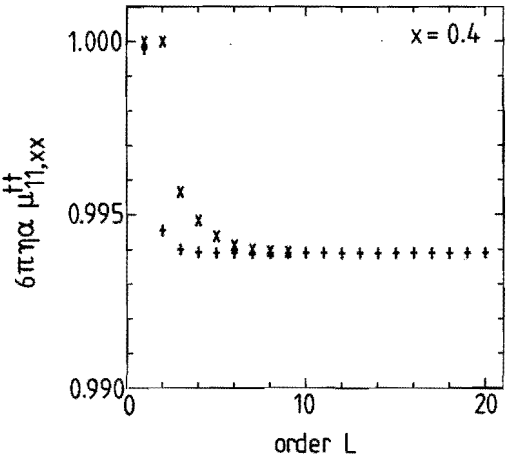


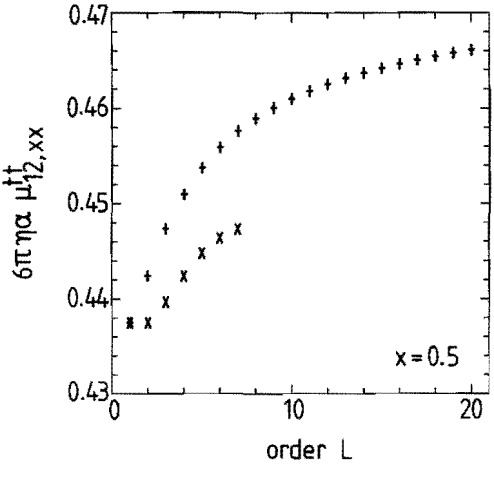
Fig. 1. *The components of the grand mobility matrix are plotted versus order L. We compare the results of Schmitz and Felderhof (×) with our results (+).*


0.14
0.13
0.12
$8\pi\eta a^3 \mu^{rr}_{12,zz}$
x = 0.5
0
10
20
order L


0.0642
0.0640
$8\pi\eta a^3 \mu^{rr}_{12,zz}$
x = 0.4
0
10
20
order L


1.00
0.98
0.96
0.94
$6\pi\eta a\ \mu^{tt}_{11,xx}$
x = 0.5
0
10
20
order L


1.000
0.995
0.990
$6\pi\eta a\ \mu^{tt}_{11,xx}$
x = 0.4
0
10
20
order L


0.47
0.46
0.45
0.44
0.43
$6\pi\eta a\ \mu^{tt}_{12,xx}$
x = 0.5
0
10
20
order L

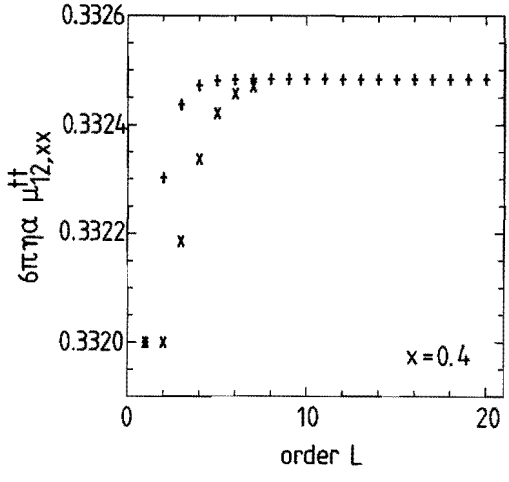

0.3326
0.3324
0.3322
0.3320
$6\pi\eta a\ \mu^{tt}_{12,xx}$
x = 0.4
0
10
20
order L

Fig.1 (cont.).

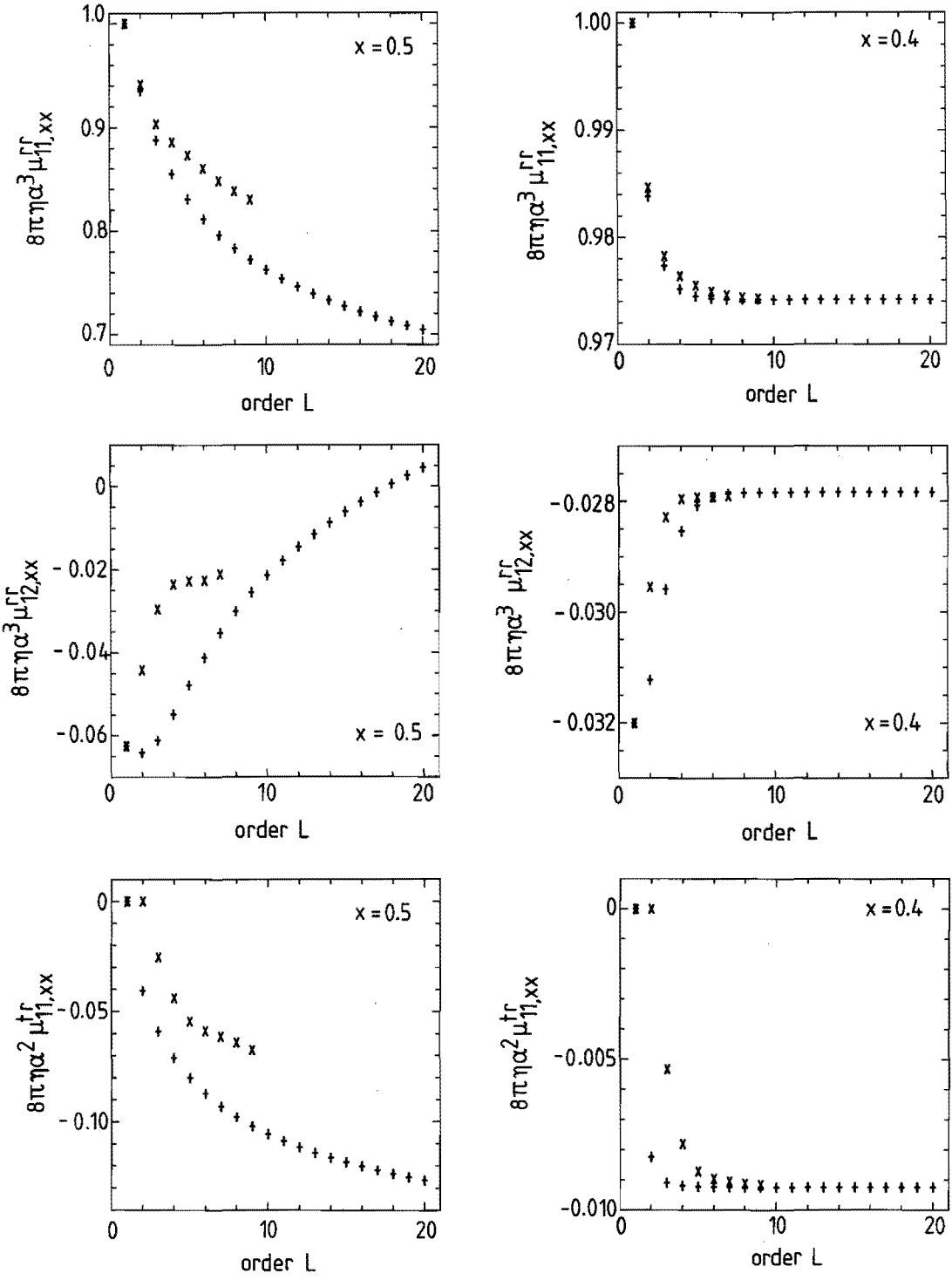

x = 0.5
x = 0.4
order L
$8\pi\eta\alpha^3\mu^{rr}_{11,xx}$
$8\pi\eta\alpha^3\mu^{rr}_{12,xx}$
$8\pi\eta\alpha^2\mu^{tr}_{11,xx}$

Fig.1 (cont.).

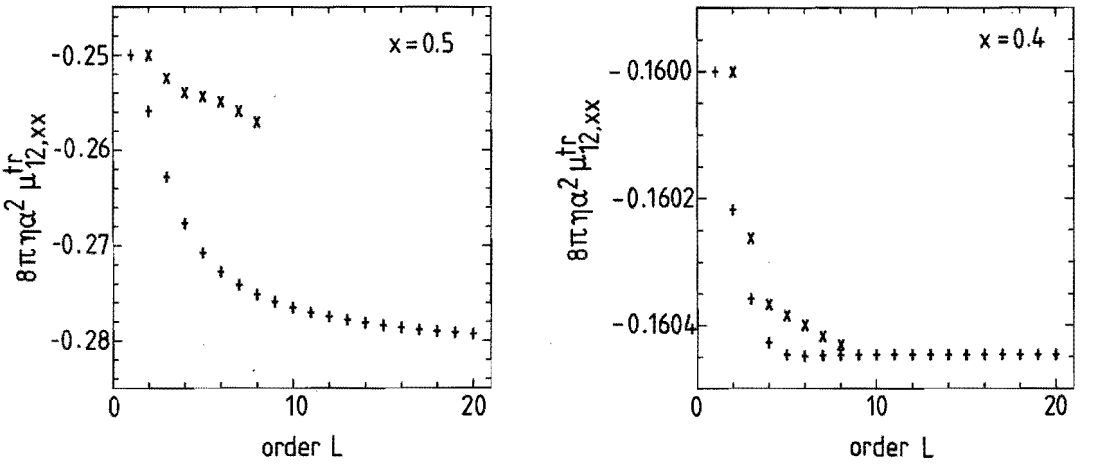


Fig.1 (cont.).

convergence behaviour of these results is, as expected, between those shown in fig.1. We cannot compare most of the components of the grand mobility matrix with exact analytical results for the simple reason that these results are not available but Batchelor tabulated some exact results for mobility coefficients in the case the two particles are acted on by equal forces parallel to and perpendicular to the line of centers (z–axis) respectively [10]. In table I we compare our results for some values of L with the exact values (in the rows labeled with $L=\infty$). In this table, $\mu_o=1/6\pi\eta_o a$, $\mu^t_{zz}=\mu^{tt}_{11,zz}+\mu^{tt}_{12,zz}$ and $\mu^t_{xx}=\mu^{tt}_{11,xx}+\mu^{tt}_{12,xx}$. The rate of convergence is comparable to the one obtained by Ladd. He has also used a direct inversion method based on the theory of Mazur and van Saarloos [3]. We can also study the mobility coefficients in case the two particles are acted on by equal torques parallel to and perpendicular to the line of centers (z–axis) respectively. In table II we compare the convergence of the mobility coefficients with increasing L with limiting values

TABLE I

R/a	L	μ^t_{zz}/μ_o	μ^t_{xx}/μ_o	R/a	L	μ^t_{zz}/μ_o	μ^t_{xx}/μ_o
2.0000	2	1.5564	1.4160	2.6749	2	1.4706	1.3032
	4	1.5503	1.4119		4	1.4662	1.3029
	6	1.5501	1.4102		∞	1.4662	1.3029
	8	1.5501	1.4089				
	∞	1.5500	1.3799	3.0862	2	1.4264	1.2587
					4	1.4236	1.2586
2.0049	2	1.5557	1.4150		∞	1.4236	1.2586
	4	1.5496	1.4109				
	6	1.5494	1.4094	4.0000	2	1.3482	1.1951
	8	1.5494	1.4081		4	1.3472	1.1950
	∞	1.5494	1.4027		∞	1.3472	1.1950
2.0907	2	1.5438	1.3972	6.0000	2	1.2428	1.1273
	4	1.5378	1.3946		4	1.2427	1.1273
	6	1.5376	1.3939		∞	1.2427	1.1273
	8	1.5376	1.3936				
	∞	1.5376	1.3933	8.0000	2	1.1847	1.0947
					∞	1.1847	1.0947
2.2553	2	1.5219	1.3661				
	4	1.5161	1.3649				
	6	1.5160	1.3648				
	∞	1.5160	1.3648				

of the mobilities produced by our method with large values of L (in the rows labeled with $L=\infty$). In this table, $\mu_o=1/8\pi\eta_o a^3$, $\mu^r_{zz}=\mu^{rr}_{11,zz}+\mu^{rr}_{12,zz}$ and $\mu^r_{xx}=\mu^{rr}_{11,xx}+\mu^{rr}_{12,xx}$.
We can conclude that the μ^r_{zz}/μ_o converge fast if L increases. The μ^r_{xx}/μ_o converge fast for increasing L if $R/a \geq 2.1$ but convergence is poor if $R/a < 2.1$. One can understand the convergence behaviour of μ^r_{xx}/μ_o by considering the friction forces between the two particles when they approach each other. The particles have equal angular velocities which are perpendicular to the z–axis. For that reason the particle surfaces in the region of contact move in opposite directions which is not the case when the particles move with the same velocities or when they rotate with the same angular velocities parallel to the z–axis. The more the particles approach each other the higher the gradient in the fluid velocity will be and consequently the bigger the friction forces. This effect is strongly marked in the case of touching spheres (R/a=2) where we are not able to calculate the limiting value for

TABLE II

R/a	L	μ^r_{zz}/μ_o	μ^r_{xx}/μ_o	R/a	L	μ^r_{zz}/μ_o	μ^r_{xx}/μ_o
2.0000	2	1.1146	0.8709	2.6749	2	1.0511	0.9637
	4	1.1095	0.7999		4	1.0508	0.9604
	6	1.1092	0.7702		6	1.0508	0.9602
	8	1.1092	0.7530		∞	1.0508	0.9602
	∞	1.1092	(0.6516)				
				3.0862	2	1.0337	0.9787
2.0049	2	1.1139	0.8725		4	1.0336	0.9777
	4	1.1089	0.8042		6	1.0336	0.9776
	6	1.1086	0.7774		∞	1.0336	0.9776
	8	1.1086	0.7630				
	∞	1.1086	0.7311	4.0000	2	1.0156	0.9913
					4	1.0156	0.9911
2.0907	2	1.1020	0.8964		∞	1.0156	0.9911
	4	1.0984	0.8591				
	6	1.0982	0.8522	6.0000	2	1.0046	0.9976
	8	1.0982	0.8508		∞	1.0046	0.9976
	∞	1.0982	0.8503				
				8.0000	2	1.0020	0.9990
2.2553	2	1.0830	0.9269		∞	1.0020	0.9990
	4	1.0812	0.9112				
	6	1.0810	0.9099				
	8	1.0810	0.9098				
	∞	1.0810	0.9098				

μ^r_{xx}/μ_o. The value in parentheses in table II is the calculated value for μ^r_{xx}/μ_o for L=150. Lubrication theory, according to Jeffrey and Onishi, predicts a value 0.534 [1].

There is a well known problem with the results presented here (and all the results obtained by the reflection method) because for $0 \leq (\frac{1}{x} - 2) \leq 10^{-3}$ there is a discrepancy with lubrication theory (see e.g. ref.[11]). However, in the case of suspensions, with particle radii of the order of 10^{-6} to 10^{-7}m or less, the range where lubrication theory is valid and relevant is of the order of 10 Ångstroms or less and in that range we cannot use hydrodynamic theories, neither ours nor the lubrication theory, anyway.

3.4 Translational and rotational self–diffusion

With the help of the grand mobility matrix it is possible to calculate the short time translational self–diffusion tensor D_s^t and the short time rotational self–diffusion tensor D_s^r of suspensions. These quantities can be used to describe the diffusion of a single test particle on a time scale in which the configuration of the particles remains nearly constant. These diffusion tensors are defined in the following way:

$$D_s^t = \frac{k_B T}{N} < \sum_{i=1}^{N} \mu_{ii}^{tt} >_c = k_B T <\mu_{11}^{tt}>_c , \tag{3.16}$$

$$D_s^r = \frac{k_B T}{N} < \sum_{i=1}^{N} \mu_{ii}^{rr} >_c = k_B T <\mu_{11}^{rr}>_c , \tag{3.17}$$

where N is the number of particles in the suspension, k_B is Boltzmann's constant, T is the absolute temperature and $<..>_c$ denotes an average over all configurations of the N particles inside a volume V. In the case of a dilute suspension we take into account two particle interactions only and the average over the configuration of the particles can be carried out with the help of the pair distribution function $g(\underline{R})$ which has up to order $\varphi=\frac{4}{3}\pi a^3 n_o$ the following form [12]:

$$g(\underline{R}) = \begin{cases} 0 & ; |\underline{R}|<2a \\ 1 + \varphi(8 - 3\frac{R}{a} + \frac{1}{16}(\frac{R}{a})^3) & ; 2a \le |\underline{R}| \le 4a \\ 1 & ; |\underline{R}|>4a \end{cases} , \tag{3.18}$$

We can now write for D_s^t

$$D_s^t = D_o^t\Big[I + n_o\int_{\mathbb{R}^3}(6\pi\eta_o a\mu_{11,zz}^{tt} - 1)\hat{R}\hat{R}\, g(\underline{R})d\underline{R} + n_o\int_{\mathbb{R}^3}(6\pi\eta_o a\mu_{11,xx}^{tt} - 1)(I - \hat{R}\hat{R})g(\underline{R})d\underline{R}\Big] \tag{3.19}$$

$$= D_o^t I\Big[1 + \frac{4\pi}{3}n_o\int_{2a}^{\infty}\Big[6\pi\eta_o a(\mu_{11,zz}^{tt} + 2\mu_{11,xx}^{tt}) - 3\Big]R^2 g(R)dR\Big] ,$$

where $D_o^t = k_B T/(6\pi\eta_o a)$, $n_o = N/V$, I is the identity tensor and $g(R) = g(|\underline{R}|)$. The

tensor $\hat{\mathbf{R}}\hat{\mathbf{R}}$ contains the orientational configuration of the particle pair; for our calculations of the grand mobility matrix we have used the special configuration $\hat{\mathbf{R}}\hat{\mathbf{R}} = \hat{\mathbf{e}}_z\hat{\mathbf{e}}_z$. In all our calculations we have expressed the components of the grand mobility matrix as a function of the dimensionless parameter x=a/R and as a consequence we can write for $\mathbf{D}_s^t$

$$(3.20) \qquad \mathbf{D}_s^t = \mathbf{D}_o^t\mathbf{I}\left[1 + \varphi \int_0^{\frac{1}{2}} \left[6\pi\eta_o a(\mu_{11,zz}^{tt}(x)+2\mu_{11,xx}^{tt}(x))-3\right]\frac{g(x)}{x^4}\,dx\right] .$$

The function g(x) is the pair distribution function as a function of the parameter x. For $\mathbf{D}_s^r$ we obtain in an analogous way

$$(3.21) \qquad \mathbf{D}_s^r = \mathbf{D}_o^r\mathbf{I}\left[1 + \varphi \int_0^{\frac{1}{2}} \left[8\pi\eta_o a^3(\mu_{11,zz}^{rr}(x)+2\mu_{11,xx}^{rr}(x))-3\right]\frac{g(x)}{x^4}\,dx\right] ,$$

where $D_o^r = k_B T/(8\pi\eta_o a^3)$. Both self–diffusion tensors can now be calculated numerically as a function of the volume fraction φ, often called a virial expansion, and the resulting expressions for $\mathbf{D}_s^t$ and $\mathbf{D}_s^r$ are respectively

$$(3.22) \qquad \mathbf{D}_s^t = \mathbf{D}_o^t\mathbf{I}(1 - 1.83\varphi - 1.13\varphi^2) ,$$

$$(3.23) \qquad \mathbf{D}_s^r = \mathbf{D}_o^r\mathbf{I}(1 - 0.63\varphi - 1.02\varphi^2) .$$

It is important to note that three particle interactions give, in the case of $\mathbf{D}_s^t$, a significant contribution to the short time self–diffusion tensor of the order φ^2 (see ref. [12] and chapter 5). In the case of $\mathbf{D}_s^r$ we expect that three particle interactions are less important. We can explain this different behaviour by comparing the following expressions for $x << \frac{1}{2}$ [7]:

$$6\pi\eta_o a(\mu_{11,zz}^{tt}(x)+2\mu_{11,xx}^{tt}(x))-3 \simeq O(x^4) , \quad 8\pi\eta_o a^3(\mu_{11,zz}^{rr}(x)+2\mu_{11,xx}^{rr}(x))-3 \simeq O(x^6) .$$

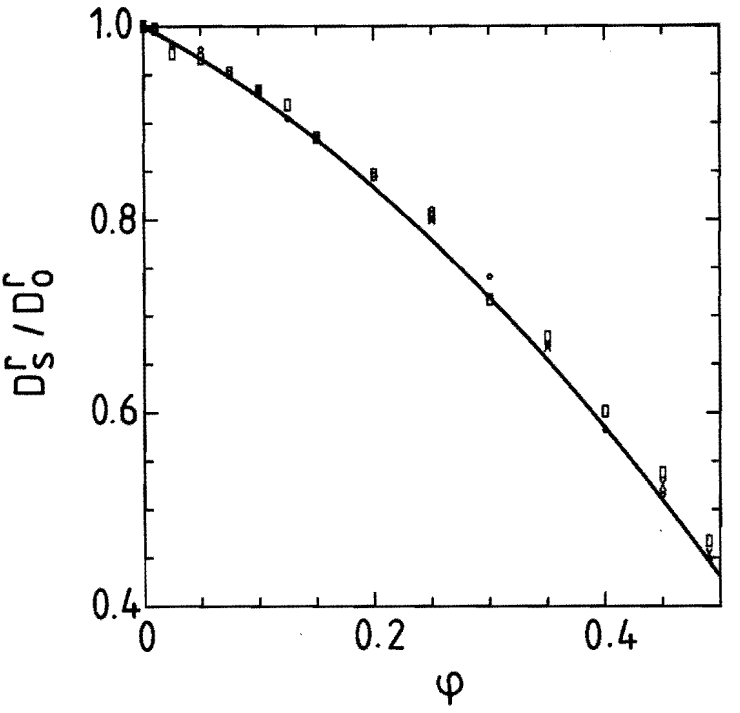


Fig.2. *The short time rotational self–diffusion coefficient, normalized with D_o^r, is plotted versus φ, the volume fraction. The solid curve represents our result, eq. (3.23), and the rectangles, circles and crosses represent simulation results of Phillips et al.*

We see that the translational expression and thus D_s^t (see eq. (3.20)) will be more sensitive to hydrodynamic interactions than their rotational counterparts. We compare our result of D_s^r (eq. (3.23)) with computer simulation results of Phillips et al. [13]. We have plotted their results combined with our result of D_s^r/D_o^r in fig. 2.

We compare the results for the first order virial coefficients of the translational and rotational self–diffusion tensors, $d_1^t=-1.83$ and $d_1^r=-0.63$ respectively, with the results for these coefficients, $d_{1,rfl}^t$ and $d_{1,rfl}^r$, obtained by Cichocki and Felderhof [14] in table III and IV respectively. We use the same criterion as mentioned above for the comparison of the components of the grand mobility matrix. We can conclude that our first order virial

TABLE III

L	d_1^t	$d_{1,\mathrm{rfl}}^t$
7	−1.819	−1.809
25	−1.831	−1.829
50	−1.832	−1.830
75	−1.832	−1.831
100	−1.832	–
∞	–	−1.831

TABLE IV

L	d_1^r	$d_{1,\mathrm{rfl}}^r$
6	−0.590	−0.544
24	−0.628	−0.614
49	−0.631	−0.624
74	−0.632	−0.627
100	−0.633	–
∞	–	−0.630

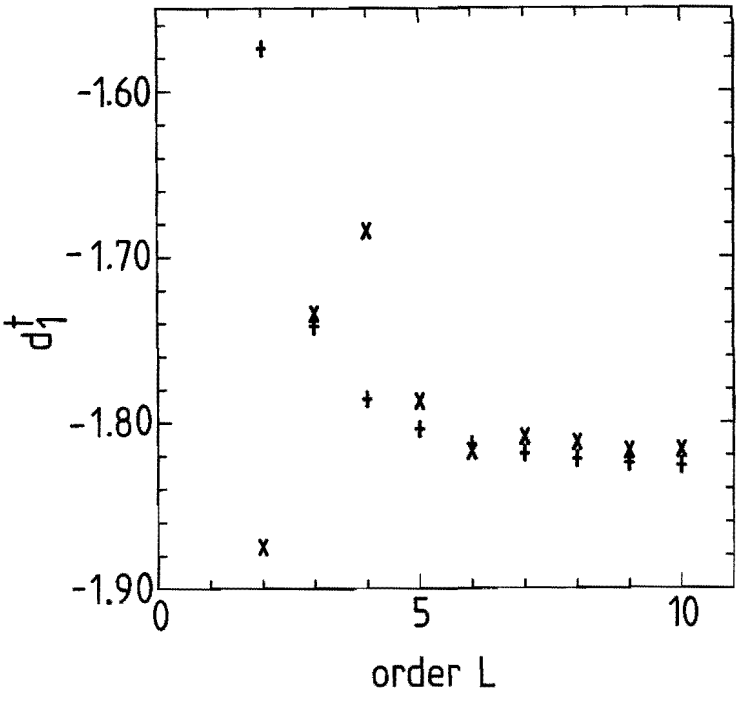


Fig.3. *The first order virial coefficient d_1^t of the normalized short time translational self–diffusion coefficient, D_s^t/D_o^t, is plotted versus order L. Again we compare the results of Schmitz and Felderhof (×) with our results (+).*

coefficient of D_s^t does not converge much faster than the result of Cichocki and Felderhof but our first order virial coefficient of D_s^r converges more quickly to a slightly lower value than the result of Cichocki and Felderhof. The first order virial coefficients calculated by the presented method converge monotonously to their final values but if we study the behaviour of $d_{1,rfl}^t$ for $L \leq 10$ we see that the first order virial coefficient for D_s^t obtained by using the reflection method has a poor convergence behaviour. See the results for d_1^t and $d_{1,rfl}^t$ in fig. 3. This behaviour can be explained by looking at the convergence behaviour of $\mu_{11,zz}^{tt}$ and $\mu_{11,xx}^{tt}$ (fig.1).

3.5 Translational and rotational sedimentation

Finally we will have a look at the short time effective diffusion coefficient $D_{eff}^t(k)$ which describes the initial decay of the dynamic structure factor F(k,t) at t=0. The dynamic structure factor F(k,t) is the quantity that can be measured by inelastic light scattering experiments on suspensions and has the following form [15]:

$$F(k,t) = S(k)\exp(-D(k,t)k^2t)\,, \tag{3.24}$$

with S(k) the static structure factor which is defined as follows:

$$S(k) = 1 + n_o \int_{\mathbb{R}^3} (g(\underline{R})-1)e^{i\underline{k}\cdot\underline{R}}d\underline{R}\,. \tag{3.25}$$

With the help of eq. (3.24) we can write for the short time effective diffusion coefficient $D_{eff}^t(k) = D(k,0)$ [15,16]

$$D_{eff}^t(k) = \frac{-1}{k^2S(k)}\frac{\partial F(k,t)}{\partial t}\bigg|_{t\downarrow 0} = \frac{k_BT}{NS(k)}\sum_{\substack{i=1\\j=1}}^{N} <\hat{k}\cdot\mu_{ij}^{tt}\cdot\hat{k}\exp(i\underline{k}\cdot\underline{R}_{ij})>_c\,, \tag{3.26}$$

where $<..>_c$ denotes again an average over all configurations of the N particles inside a volume V and $\underline{k}$ is a wavevector with direction $\hat{k}$. If we take two particle interactions into account only we can write

$$D^t_{eff}(k) = \frac{D^t_s}{S(k)} + \frac{k_B T}{S(k)} <\hat{k}\cdot\mu^{tt}_{12}\cdot\hat{k}\cos(\underline{k}\cdot\underline{R})>_c \,. \tag{3.27}$$

We are interested in the first order virial coefficient of $D^t_{eff}(k)$, which is, of course, a function of the magnitude of the wavevector $\underline{k}$. For this calculation the simplest form of the pair distribution function suffices namely $g(\underline{R})=0$ if $|\underline{R}|<2a$ and $g(\underline{R})=1$ elsewhere. The static structure factor is then

$$S(k) = 1 - \varphi\frac{6}{k^2a^2}\left[\frac{\sin(2ka)}{2ka} - \cos(2ka)\right] \,. \tag{3.28}$$

The mobility tensor μ^{tt}_{12} is known so that the configuration average can be calculated. We do this by splitting off the Oseen part of the mobility tensor in the following way:

$$\mu^{tt}_{12} = \frac{1}{6\pi\eta_o a}\frac{3a}{4R}(I+\hat{R}\hat{R}) + \nu^{tt}_{12} \,. \tag{3.29}$$

The first term of the r.h.s. of eq. (3.29) into eq. (3.27) gives an integral that can be evaluated analytically in the way Fijnaut has suggested [17]. The remaining part of the r.h.s. of eq. (3.29) gives an integral that can be calculated numerically. In the limit $ka\to\infty$ the short time effective diffusion coefficient $D^t_{eff}(k)$ becomes the short time self–diffusion coefficient D^t_s and in the limit $ka\to 0$ $D^t_{eff}(k)$ becomes the short time collective diffusion coefficient D^t_c. The calculation of the first order virial coefficient of $D^t_{eff}(k)$ gives the following expression for D^t_c:

$$D^t_c = D^t_o(1 + 1.453\varphi) \,. \tag{3.30}$$

In fig. 4 we have plotted $D^t_{eff}(k)S(k)/D^t_o$ for three values of the volume fraction φ as a function of the dimensionless parameter ka. Comparison with the results of Beenakker and Mazur [18] shows that our results are in good agreement if $\varphi \leq 0.1$ but if $\varphi > 0.1$ there are great discrepancies between our results and theirs, especially in the case $ka \leq 2$. Thus for larger values of φ we have to take into account the three and more particle interactions. We can define the sedimentation velocity of a suspension by [18]:

$$U_s/U_o = \lim_{k \to 0} D^t_{eff}(k)S(k)/D^t_o . \tag{3.31}$$

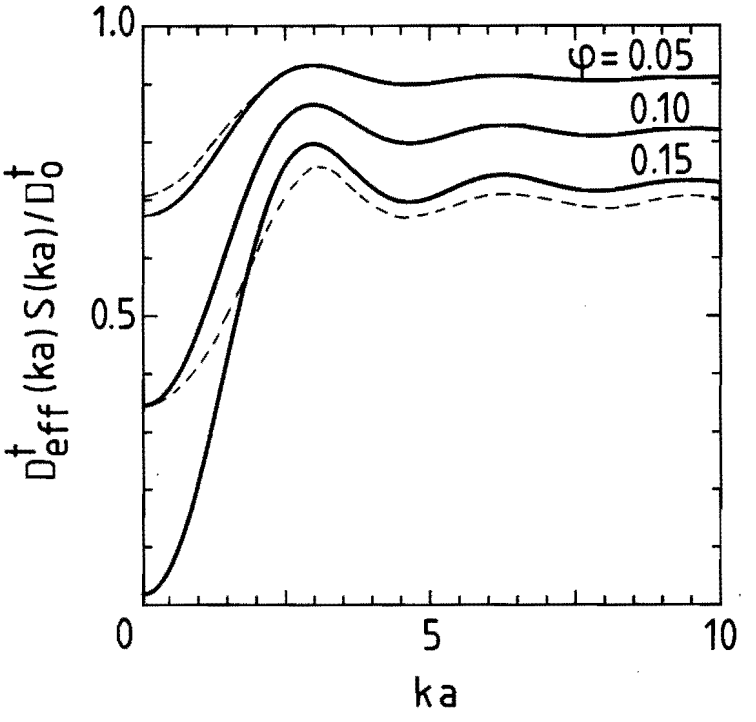


Fig.4. *Wave vector dependence of $D^t_{eff}(ka)S(ka)/D^t_o$ for three values of φ. The solid curves are our results. We have also plotted the results of Beenakker and Mazur for $\varphi=0.05$ and $\varphi=0.15$ (the dashed curves).*

Up to second order in φ, by using eq. (3.18) for the pair distribution function $g(\underline{R})$:

$$U_s/U_o = 1 - 6.547\varphi + 12.51\varphi^2 , \tag{3.32}$$

with U_s the sedimentation velocity of the suspension and U_o the sedimentation velocity of a single particle in the same fluid. The first order virial coefficient is in agreement with the result of Batchelor [10]. The second order virial coefficient should be improved by including three particle hydrodynamic interactions. The improved virial expansion is presented in chapter 5.

In an analogous way we can calculate the rotational counterpart Ω_s of the sedimentation velocity U_s. We need to know $D^r_{eff}(k)$, which is the rotational counterpart of $D^t_{eff}(k)$ (see eq. (3.27)), and obtain the following expression:

$$\Omega_s/\Omega_o = \lim_{k\to 0} D^r_{eff}(k)S(k)/D^r_o = 1 - 1.52\varphi - 0.79\varphi^2 . \tag{3.33}$$

We have again used eq. (3.18) for the pair distribution function $g(\underline{R})$. The second order virial coefficient includes two particle hydrodynamic interactions only. In chapter 5 we present the result of this coefficient where the three particle contribution is included. We can conclude from eq. (3.33) that $\Omega_s/\Omega_o = 0$ if $\varphi \approx 0.52$. Unfortunately there are no experimental results available to compare our result of Ω_s with. The rotational velocities Ω_s are important in the case of small magnetic colloidal particles rotating in an applied magnetic field. There is, however, a theoretical result available for Ω_s. Zuzovsky et al. calculated this quantity for an SC lattice of rotating spheres [19]:

$$\Omega_s/\Omega_o = 1 - \varphi . \tag{3.34}$$

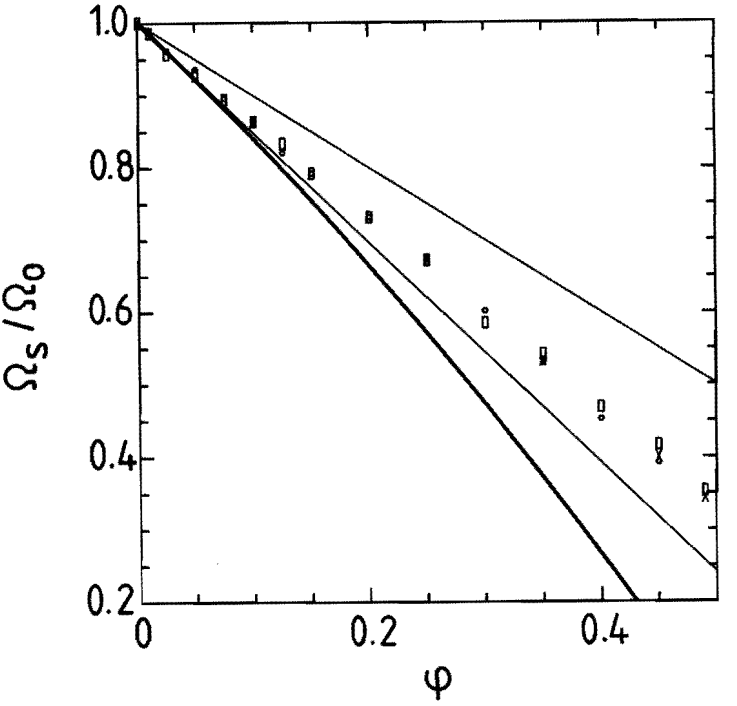


Fig.5. *The rotational velocity, normalized by its infinite dilution value Ω_o, is plotted versus φ. The bold solid curve represents our result, eq. (3.33), and the rectangles, circles and crosses represent simulation results of Phillips et al. The thin solid curve below the simulation results represents the linear part of eq. (3.33) and the upper thin solid curve is the result of Zuzovsky et al. (eq. (3.34)).*

They assumed that this result is also valid for disordered systems if the volume fraction φ is very small. If we compare our result of Ω_s with the result of Zuzovsky et al. of this quantity we see a great discrepancy. We also compare our result of Ω_s/Ω_o with computer simulation results of Phillips et al. [13]. We have plotted our results and the results of the simulations in fig. 5 and see that there also a discrepancy exists. We expect that eq. (3.33) will be modified by including three and more particle interactions in contrast to eq. (3.23) which expresses the rotational self–diffusion coefficient as a function of volume fraction.

We can understand this difference if we compare the behaviour of $\mu^{rr}_{11,\alpha\alpha}$ and $\mu^{rr}_{12,\alpha\alpha}$, with $\alpha\in\{x,y,z\}$, for great interparticle distances. In this situation we can use the results of Jones and Schmitz [7]:

$$8\pi\eta_o a^3\mu^{rr}_{11,\alpha\alpha} = 1 + O(x^6)\,, \quad 8\pi\eta_o a^3\mu^{rr}_{12,\alpha\alpha} = O(x^3)\,.$$

We see that $\mu^{rr}_{12,\alpha\alpha}$ is more sensitive to hydrodynamic interactions and so will be Ω_s/Ω_o. On the other hand we expect that the simulation results of Phillips et al. do not incorporate the three particle interactions completely. We come to this point in chapter 5 where we present the results of a study of three particle hydrodynamic interactions. This study gives us more insight in the way how the results presented above should be modified.

3.6 Conclusion

To test the presented method we solved the two particle problem and compared the results with some results from the literature. It is shown that our method leads to good results and reproduces first order virial coefficients of D^t_s (eq. (3.22)), D^r_s (eq. (3.23)), D^t_c (eq. (3.30)) and U_s/U_o (eq. (3.32)), which are already known, with great accuracy. We were also able to calculate some new results such as the second order virial coefficient for D^r_s (eq. (3.23)) and the virial expansion of Ω_s/Ω_o to second order in φ (eq. (3.33)). The next step in this study is the extension of the calculations by taking into account the three particle interactions. This makes calculation of the higher order virial coefficients of the diffusion coefficients possible. Before we come to this point we present an alternative approach to the calculation of the high frequency effective viscosity of hard sphere suspensions based on the ideas of Saito. In chapter 7 we shall use the same ideas to study the effect of the two particle interactions on the correlation functions of Brownian

particles. In that case it is necessary to extend this method and to solve the time dependent linear Navier–Stokes equation.

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Chapter 4 THE EFFECTIVE VISCOSITY OF HARD SPHERE SUSPENSIONS

4.1 Introduction

In recent years several attempts have been made to calculate, on theoretical grounds, the high frequency effective viscosity η^{∞}_{eff} (in the following abbreviated to effective viscosity) of a suspension of undeformable spherical particles, in a fluid with shear viscosity η_o, as function of the volume fraction φ of suspended particles. The effective viscosity of a suspension of hard spheres can be measured experimentally by studying the behaviour of this suspension in an oscillating shear flow at high frequencies (see e.g. the measurements of van der Werff, de Kruif, Blom and Mellema [1]). At high frequencies, the effective viscosity η^{∞}_{eff} will be determined by hydrodynamic interactions between the spherical particles only, because the effects of Brownian motion can be neglected. At lower frequencies Brownian motion becomes important as shown experimentally by e.g. van der Werff et al. [1] and theoretically by the work of e.g. Batchelor [2], who calculated η^{o}_{eff}, the steady shear limit of the effective viscosity. In the high frequency limit we can furthermore assume that the pair distribution function $g(\underline{R})$ is isotropic, because within this limit it is not very likely that the oscillating shear flow disturbs the equilibrium pair distribution function. The behaviour of η^{∞}_{eff} at low volume fraction of suspended particles is well understood and the virial expansion of η^{∞}_{eff}, to second order in φ, is

$$\eta^{\infty}_{eff} = \eta_o(1 + C_1\varphi + C_2\varphi^2) \,. \tag{4.1}$$

The first order virial coefficient C_1 was already calculated by Einstein in the beginning of

this century [3]. The value is $C_1=\frac{5}{2}$. Experiments with suspensions of spherical particles show that it is necessary to incorporate higher order corrections if $\varphi>0.05$. For that reason many attempts were made in the last few decades to calculate the second order virial coefficient C_2 and, related to this number, the Huggins coefficient k_h with $k_h=\frac{4}{25} C_2$. This coefficient was studied by Peterson and Fixman, who derived the value $k_h=0.69$ [4]. Later on Batchelor and Green determined C_2 in an exact way [5]. Their result is $C_2 = 5.2 \pm 0.3$. They came to this coefficient by taking into account two particle hydrodynamic interactions between suspended particles in a shear flow only. For this calculation they used the simplest form of the pair distribution function i.e. exclusion of particle overlap (hard spheres). Recently Cichocki and Felderhof determined a more accurate value for the term quadratic in volume fraction of η^{∞}_{eff}, $C_2 = 5.00$ [6]. Their calculations are based upon a multipole expansion of the hydrodynamic interactions [7]. The difference between the result of Batchelor and Green on the one hand and Cichocki and Felderhof on the other can be explained by realizing that Cichocki et al. used more accurate hydrodynamic functions to evaluate C_2. Russel and Gast extended the formalism of Batchelor and Green by including a volume fraction dependent equilibrium pair distribution function [8].

There exist other expressions in the literature describing the effective viscosity. One of the alternatives is the expression derived by Saito [9,10], which is:

$$\eta^{\infty}_{eff} = \eta_o(1 + \tfrac{5}{2}\frac{\varphi}{(1-\varphi)}) . \qquad (4.2)$$

Cichocki, Felderhof and Schmitz have derived a relation for η^{∞}_{eff} with the help of a cluster expansion [11]. Their result takes a form similar to the Saito–formula (eq. (4.2)) and is obtained by including the two–body approximation in the cluster expansion only. The expression for the effective viscosity has a pole for $\varphi=0.364$, a relatively low volume fraction. To bring into line the theoretical expression with the experimental results, they concluded that higher order correction terms in the cluster expansion should be taken into

account to shift the pole to a higher volume fraction. Beenakker obtained the effective viscosity using an expansion in density fluctuation correlation functions [12]. His numerical result, taking into account many particle hydrodynamics, is in good agreement with the experimental results of van der Werff et al. for $\varphi \lesssim 0.45$ [1]. Beenakker did not present results for higher volume fractions because he expected that those would be less accurate. The list of results for $\eta^{\infty}_{\text{eff}}$ mentioned above is not complete and could be extended by work of other authors [13–17]. Several authors, like Mellema and Willemse [13] and Bedeaux [14], treated the suspension as a mixture of two fluids with different shear viscosities. To describe suspensions they assumed that the viscosity of one fluid, present with volume fraction φ, should be infinitely large. Their result in this limit is

$$\eta^{\infty}_{\text{eff}} = \eta_{\text{o}}\left(1 + \frac{\frac{5}{2}\varphi}{(1 - \frac{5}{2}\varphi)}\right) . \tag{4.3}$$

We see in this equation that the effective viscosity has a pole for $\varphi=0.4$. This seems contradictory to the experimental results. The same formula was earlier derived by Lundgren [15].

Finally we focus attention on some numerical results. Some years ago Brady and Bossis developed a method for simulating a system consisting of spherical particles in shear flow. They called it "Stokesian dynamics simulation" (for a summary of the general Stokesian dynamics method we refer to a paper of Brady and Bossis [18]). In a later article Phillips, Brady and Bossis present computer simulation results of the effective viscosity [19]. We also mention here the numerical results for $\eta^{\infty}_{\text{eff}}$ of Ladd [20,21]. All these numerical results for the effective viscosity can be used to compare theoretical results with.

In this article we present a method to determine the effective viscosity theoretically. The final result is

$$\eta^{\infty}_{\text{eff}} = \eta_o\left(1 + \frac{\left(\frac{5}{2}\varphi + 1.42\varphi^2\right)}{\left(1 - 1.42\varphi\right)}\right) \tag{4.4}$$

and can be obtained in a way similar to Saito's way of deriving his expression for $\eta^{\infty}_{\text{eff}}$ (eq. (4.2)). This expression will be discussed in section 4.3. Our theoretical expression is in good agreement with experimental results of van der Werff et al. [1] for volume fractions up to 0.6. This result is remarkable because we incorporated two particle hydrodynamic interactions only. Eq. (4.4) also agrees reasonably well with computer simulation results. It is important to note that three and more particle hydrodynamic interactions are important for higher volume fractions ($\varphi \geq 0.2$) but we expect that the contributions of these higher order corrections are more subtle than with the commonly used expressions to describe the effective viscosity (viz. eq. (4.1)). The advantage is that the final result tends faster to the experimental results and simulation data if many particle hydrodynamic interactions are included in comparison with the quadratic virial expansion, eq. (4.1). Future research should find out if the presented procedure can also be followed in the case of other problems. We can think e.g. of the steady shear limit of the effective viscosity, η^{o}_{eff}. Finally we want to point out that eq. (4.4) has a pole for $\varphi \approx 0.70$, which is nearly equal to the maximum packing fraction of a hard sphere system.

In this chapter we present the derivation of eq. (4.4); the result will be discussed in section 4.3. We end this chapter with some concluding remarks.

4.2 The derivation of the effective viscosity

Our study of the effective viscosity is in line with the ideas presented by Saito [9] because we try to find a relation for the effective viscosity $\eta^{\infty}_{\text{eff}}$ assuming that the bulk stress on the fluid remains constant independent of the number of suspended particles. We

can achieve this by keeping in mind a special experimental setup with which the physical ideas become more clear. Imagine a viscosimeter, which is an apparatus of Couette, where the radii of the cylinders are considered infinite compared with the distance between the inner and outer cylinder. We can regard the surface of the two cylinders as two parallel planes. We assume that the distance between the two planes is large compared to the particle dimensions, so we can ignore wall effects. In this viscosimeter we put a fluid, which is the ambient fluid of the suspension, with viscosity η_o, and we exert an oscillating torque $\underline{T}_o$ on, say, the outer cylinder while the inner cylinder is kept fixed. The outer cylinder will rotate with an oscillating angular velocity $\underline{\omega}_o$. Under these conditions we can conclude that, between the two planes, an oscillating shear flow exists, which can be described with a rate of strain tensor. This experimental setup is a special case because of the geometry used, but in general we can introduce the (oscillating) rate of strain tensor $\mathbf{G}_o$, independent of the geometry used. In the next experiment we add some small undeformable spherical particles to the pure fluid creating a suspension with a volume fraction φ of dispersed particles. This suspension will have an effective viscosity η^{∞}_{eff}. Again we exert the same oscillating torque $\underline{T}_o$ on the outer cylinder but now the oscillating angular velocity of it, $\underline{\omega}_{eff}$, is smaller than $\underline{\omega}_o$. This is a consequence of the fluid velocity perturbations caused by the suspended particles. The rate of strain tensor of this system, assuming a fixed particle configuration, is $\mathbf{G}_{eff}$ and is effectively a volume average of the rate of strain in the system. For the general case we can write,

$$\mathbf{G}_{eff} = \frac{1}{V}\int (\nabla \underline{v}(\underline{r}))^{s} dV \,. \tag{4.5}$$

The rate of strain depends also on the configuration of the suspended particles. However, if many particles are present in a macroscopic volume V then the configuration average and the volume average yield the same result. The shear forces per unit surface on the outer cylinder of the apparatus of Couette of the experimental setup described above, are equal

in both experiments so we know the following relation between G_o and G_{eff}:

$$\eta_o G_o = \eta^{\infty}_{eff} G_{eff} . \tag{4.6}$$

The calculations to determine η^{∞}_{eff} consist of two main parts, but in both the same numerical problem has to be solved. In the first step we express the rate of strain tensor of a suspension, with a volume fraction φ of dispersed particles, in terms of the mobility matrix and the stresslets. If the system contains N force and torque free particles, then eq (2.11) implies

$$G_{oi} = \sum_{j=1}^{N} \mu^{dd}_{ij} : S_j . \tag{4.7}$$

We assume that the stresslets are independent of particle configuration. This seems a good approximation if we consider pair interactions between the particles, but at the moment it is an open question whether this approximation is a good one if we want to incorporate three and more particle interactions. Summing over i, taking the configurational average and using the assumption of constant stresslets, we have:

$$\langle \overline{G} \rangle_c = \langle \mu^{dd}_{11} + \mu^{dd}_{12} \rangle_c : \overline{S} , \tag{4.8}$$

where

$$\langle \mu^{dd}_{11} \rangle_c = \mu^{dd}_o + n_o \int_{|\underline{R}| \geq 2a} (\mu^{dd}_{11} - \mu^{dd}_o) d\underline{R} , \quad \langle \mu^{dd}_{12} \rangle_c = n_o \int_{|\underline{R}| \geq 2a} \mu^{dd}_{12} d\underline{R} ,$$

μ^{dd}_o is the pure one particle mobility, $n_o = N/V$ and $\langle \cdots \rangle_c$ denotes a configuration average. The pair correlation is simply the no–overlap condition. One should be cautious with the calculation of $\langle \mu^{dd}_{12} \rangle_c$ because the integral is conditionally convergent. We shall discuss this point later on. The bar of $\overline{G}$ and $\overline{S}$ indicates an average over particles:

$$\overline{\mathbf{G}} = \frac{1}{N} \sum_{i=1}^{N} \mathbf{G}_{oi} \,. \tag{4.9}$$

We may identify this with eq. (4.5): $\langle \overline{\mathbf{G}} \rangle_c = \mathbf{G}_{eff}$. The double dot in eqs. (4.7) and (4.8) stands for a double contraction between the fourth rank dipole–dipole mobility tensor and the stresslet.

We do not present the details of the calculation of the components of the dipole–dipole mobility matrix μ^{dd}. This calculation is more or less a technical matter. The procedure is in principle the same as the one presented in chapter 3. An important difference, however, is the fact that the particles are force and torque free. This means that $\beta^i_{1m}=0$ and $\gamma^i_{1m}=0$, with $m\in\{-1,0,1\}$, which is a simple consequence of eqs. (2.53) and (2.54). Furthermore we express the coefficients α^i_{pq}, with $p\geq 1$, β^i_{pq}, with $p\geq 2$, and γ^i_{pq}, with $p\geq 3$ (and the accompanying allowed values for the azimuthal indices q), for i=1,2, in terms of the coefficients γ^j_{2m}, $|m|\leq 2$ and j=1,2. For more details see chapter 3.

The dipole–dipole mobility matrix is made up of tensors of rank four, μ^{dd}_{ij}, and these tensors have the following structure, according to Cichocki, Felderhof and Schmitz [7], if hydrodynamic pair interactions are included (we use a slightly different notation):

$$\begin{aligned}
\mu^{dd}_{ij,\alpha\beta\mu\nu} = (\mu^{dd}_{ij,\alpha\beta\mu\nu})_o + \frac{3}{20\pi\eta_o a^3}\Bigg[& \tfrac{3}{2}A^{dd}_{ij}(R)\, \overbrace{\hat{R}_\alpha\hat{R}_\beta}^{(\alpha\beta)}\, \overbrace{\hat{R}_\mu\hat{R}_\nu}^{(\mu\nu)} \\
& + 2B^{dd}_{ij}(R)\Big[\overbrace{\delta_{\alpha\mu}\hat{R}_\beta\hat{R}_\nu}^{(\alpha\beta)(\mu\nu)} - \overbrace{\hat{R}_\alpha\hat{R}_\beta}^{(\alpha\beta)}\, \overbrace{\hat{R}_\mu\hat{R}_\nu}^{(\mu\nu)} \Big] \\
& + C^{dd}_{ij}(R)\Big[\overbrace{\delta_{\alpha\mu}\delta_{\beta\nu}}^{(\alpha\beta)(\mu\nu)} - 2\, \overbrace{\delta_{\alpha\mu}\hat{R}_\beta\hat{R}_\nu}^{(\alpha\beta)(\mu\nu)} + \tfrac{1}{2}\, \overbrace{\hat{R}_\alpha\hat{R}_\beta}^{(\alpha\beta)}\, \overbrace{\hat{R}_\mu\hat{R}_\nu}^{(\mu\nu)} \Big] \Bigg] ,
\end{aligned} \tag{4.10}$$

where $\hat{R}_\alpha = R_\alpha/R$ and i,j$\in\{1,2\}$. The symbol $\overline{}^{(\alpha\beta)}$ denotes a projection onto the symmetric and traceless part in the index pair $(\alpha\beta)$. The projected tensors in eq. (4.10) read explicitly, according to Cichocki et al. [7],

$$(4.11)\qquad \overline{\hat{R}_\alpha \hat{R}_\beta}^{(\alpha\beta)} = \hat{R}_\alpha \hat{R}_\beta - \tfrac{1}{3}\delta_{\alpha\beta}\,, \quad \overline{\delta_{\alpha\mu}\delta_{\beta\nu}}^{(\alpha\beta)}{}^{(\mu\nu)} = \tfrac{1}{2}(\delta_{\alpha\mu}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\mu}) - \tfrac{1}{3}\delta_{\alpha\beta}\delta_{\mu\nu}\,,$$

$$\overline{\delta_{\alpha\mu}\hat{R}_\beta\hat{R}_\nu}^{(\alpha\beta)}{}^{(\mu\nu)} = \tfrac{1}{4}(\delta_{\alpha\mu}\hat{R}_\beta\hat{R}_\nu+\delta_{\alpha\nu}\hat{R}_\beta\hat{R}_\mu+\delta_{\beta\mu}\hat{R}_\alpha\hat{R}_\nu+\delta_{\beta\nu}\hat{R}_\alpha\hat{R}_\mu)$$

$$-\tfrac{1}{3}(\delta_{\alpha\beta}\hat{R}_\mu\hat{R}_\nu+\hat{R}_\alpha\hat{R}_\beta\delta_{\mu\nu}) + \tfrac{1}{9}\delta_{\alpha\beta}\delta_{\mu\nu}\,.$$

Furthermore:

$$(4.12)\qquad (\mu^{dd}_{ij,\alpha\beta\mu\nu})_o = \frac{3}{40\pi\eta_o a^3}(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\mu\nu})\delta_{ij}\,.$$

The functions $A^{dd}_{ij}(R)$, $B^{dd}_{ij}(R)$ and $C^{dd}_{ij}(R)$ are the so called hydrodynamic functions, which can be determined from the set of linear equations. The determination of these functions can be achieved independently because each of them belongs to a special value of the azimuthal index m and the set of linear equations is decoupled considering these indices. The $A^{dd}_{ij}(R)$ are related to the set of linear equations for $m=0$, the $B^{dd}_{ij}(R)$ to $|m|=1$ and the $C^{dd}_{ij}(R)$ to $|m|=2$. Consequently the set of linear equations with $|m|>2$ is of no interest to us.

The lowest order solutions ($L=2$, see chapter 3) of the hydrodynamic functions result in the following expressions:

$$(4.13)\qquad A^{dd}_{11}(x) = O(x^8)\,, \quad B^{dd}_{11}(x) = O(x^8)\,, \quad C^{dd}_{11}(x) = O(x^8)$$

$$A^{dd}_{12}(x) = -5x^3+12x^5+O(x^8)\,, \quad B^{dd}_{12}(x) = \tfrac{5}{2}x^3-8x^5+O(x^8)\,, \quad C^{dd}_{12}(x) = 2x^5+O(x^8)\,,$$

where $x=\frac{a}{R}$. Our aim is now the calculation of the configuration average of the difference $(\mu_{ij}^{dd}-(\mu_{ij}^{dd})_o)$, using the simplest form of the pair distribution function, excluding particle overlap only, or $g(\underline{R})=g(|\underline{R}|)=0$ if $|\underline{R}|<2a$ and $g(|\underline{R}|)=1$ if $|\underline{R}|\geq 2a$. The configuration average is now defined as

$$(4.14) \qquad <(\mu_{ij}^{dd}-(\mu_{ij}^{dd})_o)>_c \equiv n_o \int_{|\underline{R}|\geq 2a} (\mu_{ij}^{dd}-(\mu_{ij}^{dd})_o) d\underline{R} ,$$

with $n_o=N/V$ the particle density. In the following we denote a configuration average with $<\cdots>_c$. This averageing procedure must be done very carefully because of the appeareance of conditionally convergent integrals. This has to do with the terms proportional to x^3 in the expressions for $A_{12}^{dd}(R)$ and $B_{12}^{dd}(R)$ (see eq. (4.13)). If we consider the hydrodynamic functions with terms up to x^5 only we arrive at the situation already considered by Saito. Proper volume averageing gives the so called Saito contribution, which gives rise to the virial coefficient $c_S=-1$ [9]. It is not the most elegant way to solve the problem of conditionally convergent integrals. However, other studies have confirmed the value of c_S. This coefficient comes out in work of other authors, e.g. Felderhof reproduced it using a local field argument [22,23] or from a virtual overlap contribution to the two–body cluster integral [24]. See in this context also the work of Bedeaux, Kapral and Mazur [16]. With the theory of renormalized cluster expansions it is possible to avoid these unpleasant conditionally convergent integrals [25,26,11]. This theory confirms the value of the Saito coefficient c_S. These renormalized cluster expansions has also been used in the theory of sedimentation [27]. This kind of conditionally convergent integrals also appears in the work of Batchelor and Green although in an other form [5]. For further calculations we split off the terms proportional to x^3 and x^5 without renaming the remaining parts of the hydrodynamic functions $A_{12}^{dd}(R)$ and $B_{12}^{dd}(R)$ (we shall see below that it is not necessary). To avoid misunderstanding we shall lable the remaining part of the configurational

averages with sr, which stands for short range part. The contribution of the terms just splitted off will be represented by the Saito coefficient c_S.

It is not difficult to evaluate the angular average of the short range part of eq. (4.14) keeping R, the interparticle distance, constant. The result is

$$(4.15)\qquad <(\mu^{dd}_{ij,\alpha\beta\mu\nu}-(\mu^{dd}_{ij,\alpha\beta\mu\nu})_o)>^{sr}_{c,\Omega} \equiv \int (\mu^{dd}_{ij,\alpha\beta\mu\nu}-(\mu^{dd}_{ij,\alpha\beta\mu\nu})_o)d\Omega$$

$$= \frac{3}{20\pi\eta_o a^3} f^{dd}_{ij}(R)(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\mu\nu}) ,$$

with

$$(4.16)\qquad f^{dd}_{ij}(R) = \tfrac{2}{5}\pi\left[A^{dd}_{ij}(R)+2B^{dd}_{ij}(R)+2C^{dd}_{ij}(R)\right] .$$

We are now able to determine the double contraction between the angular averaged mobility tensor and the stresslet $\overline{S}$,

$$(4.17)\qquad <(\mu^{dd}_{ij}-(\mu^{dd}_{ij})_o)>^{sr}_{c,\Omega}:\overline{S} = \frac{3}{10\pi\eta_o a^3} f^{dd}_{ij}(R)\overline{S} .$$

The total configuration average is now

$$(4.18)\qquad <(\mu^{dd}_{ij}-(\mu^{dd}_{ij})_o)>^{sr}_{c}:\overline{S} = \tfrac{3}{5}\varphi(\frac{3}{20\pi\eta_o a^3}\overline{S})\int_0^{\frac{1}{2}}\left[A^{dd}_{ij}(x)+2B^{dd}_{ij}(x)+2C^{dd}_{ij}(x)\right]\frac{dx}{x^4} ,$$

where we have changed the variable of integration using x=a/R. Substitution of this result for the configuration averages in eq. (4.8) gives,

$$(4.19)\qquad G_{eff} = \frac{3}{20\pi\eta_o a^3}\overline{S}\left[1 + c_S\varphi + \tfrac{3}{5}\varphi\int_0^{\frac{1}{2}}\sum_{j=1}^{2}\left[A^{dd}_{1j}(x)+2B^{dd}_{1j}(x)+2C^{dd}_{1j}(x)\right]\frac{dx}{x^4}\right] .$$

The integral in eq. (4.19) can be calculated numerically and the result is: –0.694. The final result is

$$G_{eff} = \frac{3}{20\pi\eta_o a^3}(1-1.42\varphi)\bar{S} \qquad (4.20)$$

In the second step we determine $\eta_o(G_o-G_{eff})$ in terms of the stresslet $\bar{S}$. G_o is the rate of strain in the infinitely diluted suspension and G_{eff} is the volume averaged rate of strain in a suspension with a volume fraction φ of dispersed particles. In a formal notation, where the tensor contractions $M^{dd}_{ij}:\bar{S}$ are introduced as a short hand notation to describe the rate of strain of the scattered velocity fields around the two particles in terms of the stresslet $\bar{S}$ (in the case that pair interactions are included only),

$$\eta_o G_o = \eta_o G_{eff} + <M^{dd}_{11}+M^{dd}_{12}>_c:\bar{S} . \qquad (4.21)$$

With this relation and eq. (4.20) we can eliminate the stresslet $\bar{S}$. Comparison of the final relation with eq. (4.6) gives us η^{∞}_{eff}. The determination of $\eta_o(G_o-G_{eff})$, as function of volume fraction φ, is possible by studying the following quantity:

$$(\nabla \underline{v}_o(\underline{r}))^s-(\nabla \underline{v}(\underline{r}))^s = -\sum_{i=1}^{N} (\nabla \underline{v}_i(\underline{r}_i))^s \equiv (\Delta_1+\Delta_2)/\eta_o , \qquad (4.22)$$

with $\underline{v}_i(\underline{r}_i)$ a scattered velocity field defined with respect to the center of particle i (see eq. (2.25)). We have introduced N scattered velocity fields because there are N particles present in the suspension, but we study two particle hydrodynamic interactions only. The tensors Δ_1 and Δ_2 will be defined below. In the first place we have to calculate the volume average of the l.h.s. of eq. (4.22). We know the rate of strain in the pure fluid case, so the result of the volume averageing of $(\nabla \underline{v}_o(\underline{r}))^s$ is

$$(4.23) \qquad \frac{1}{V}\int (\nabla \underline{v}_o(\underline{r}))^s dV = \mathbf{G}_o \,.$$

We also know the effective rate of strain of a suspension with volume fraction φ of dispersed spherical particles. We can study this rate of strain by measuring the angular frequency $\underline{\omega}_{eff}$ of the outer cylinder of a Couette apparatus with the same torque on the outer cylinder as in the pure fluid case described above. The rate of strain is $\mathbf{G}_{eff}$ and is an volume average in the above sense (see eq. (4.23)), with $\underline{v}_o(\underline{r})$ replaced by $\underline{v}(\underline{r})$,

$$(4.24) \qquad \frac{1}{V}\int (\nabla \underline{v}(\underline{r}))^s dV = \mathbf{G}_{eff} \,.$$

We are also able to calculate the volume and configuration average of the r.h.s. of eq. (4.22). To obtain the final result we distinguish between a quasi one–particle contribution, denoted by Δ_1, and an excluded volume contribution, Δ_2. It is noteworthy that we have to consider all scattered velocity fields, but the average of the terms in the sum of eq. (4.22), concerning the fluid velocity fields, yield the same result. For convenience we calculate the expressions below by using the velocity fields $\underline{v}_1(\underline{r}_1)$ and $\underline{v}_2(\underline{r}_2)$ only; this makes no difference in the calculation of the final result. The quasi one–particle contribution can be determined very easily with the following relation:

$$(4.25) \qquad \langle \Delta_{1,eff} \rangle_c = -\eta_o n_o \int_{|\underline{r}_2| \geq a} (\nabla \underline{v}_2(\underline{r}_2))^s d\underline{r}_2 = \tfrac{1}{2} n_o \mathbf{S}$$

We call $\langle \Delta_{1,eff} \rangle_c$ a quasi one–particle contribution because the expansion coefficients of the velocity field $\underline{v}_2(\underline{r}_2)$ contain the hydrodynamic pair interactions. Our expression for the stresslet $\mathbf{S}$ follows from (4.20):

$$\bar{S} = \tfrac{20}{3}\pi\eta_o a^3 \frac{1}{(1-1.42\varphi)} G_{eff} \tag{4.26}$$

and we obtain for $<\Delta_{1,eff}>_c$

$$<\Delta_{1,eff}>_c = \tfrac{5}{2} \frac{\varphi}{(1-1.42\varphi)} \eta_o G_{eff} \tag{4.27}$$

Obviously we have not excluded the volume of the other particles to obtain eq. (4.27). The final result can be obtained by addition of the extra amount $<\Delta_{2,eff}>_c$. This extra amount is the negative value of the integral, defined in eq. (4.25), within the volume occupied by the other particles. The extra amount $<\Delta_{2,eff}>_c$ is

$$<\Delta_{2,eff}>_c = \eta_o n_o^2 \int_{|\underline{R}| \geq 2a} d\underline{R} \int_{|\underline{r}_1| \leq a} d\underline{r}_1 (\nabla \underline{v}_2(\underline{r}_1))^s , \tag{4.28}$$

with $\underline{R}$ the interparticle distance. Although we did not write down the $\underline{R}$–dependence of the integrand in the equation above it should be remembered that this dependence is implicitly assumed in the expansion coefficients $\{\alpha^2_{lm}, \beta^2_{lm}, \gamma^2_{lm}\}$. Evidently we have used the simplest form of the pair distribution function which excludes overlap of the two particles only. The integral over the volume of particle 1 can be determined easily from the following integral theorem for tensors (see e.g. ref.[28]):

$$\int_V A_{ij} dV = \int_A A_{ik} x_j n_k dA - \int_V \frac{\partial A_{ik}}{\partial x_k} x_j dV , \tag{4.29}$$

with V the enclosed volume, A the surface enclosing V and n_k a component of an outward unit vector. In our case this unit vector is pointing into the fluid because V is the volume occupied by particle 1. Define now the symmetric and traceless tensor B with components

$$B_{ij} = -\Pi_{ij}+\tfrac{1}{3}\delta_{ij}\Pi_{ll} , \tag{4.30}$$

where we used the summation convention for double indices. The tensor Π is the pressure tensor,

$$\Pi = pI-2\eta_o(\nabla \underline{v})^s . \tag{4.31}$$

It is obvious that $B = 2\eta_o(\nabla \underline{v})^s$. Combination of eqs. (4.29)–(4.31) gives, with the identity $\nabla\cdot\Pi=0$,

$$2\eta_o \int_{|\underline{r}_1|\le a} d\underline{r}_1(\nabla \underline{v}_2(\underline{r}_1))^s_{ij} = \int_{|\underline{r}_1|=a} B_{ik}x_j n_k dA = (S_1^2)_{ij} , \tag{4.32}$$

the stresslet exerted by the fluid velocity field $\underline{v}_2$ on particle 1. Substitution of this result for the integrand in eq. (4.28), use of eq. (II.13) of appendix II and using the set of linear equations (2.36)–(2.38) to express the coefficients α^2_{pq}, with $p\ge 1$, β^2_{pq}, with $p\ge 2$, and γ^2_{pq}, with $p\ge 3$ (and the accompanying allowed values for the azimuthal indices q) in terms of the coefficients γ^1_{2m}, $|m|\le 2$, we obtain after calculation of the configuration average,

$$<\Delta_{2,eff}>_c = -\varphi\frac{3}{20\pi a^3}\overline{S}\left[c_S\varphi + \tfrac{3}{5}\varphi\int_0^{\frac{1}{2}}\sum_{j=1}^{2}\left[A^{dd}_{1j}(x)+2B^{dd}_{1j}(x)+2C^{dd}_{1j}(x)\right]\frac{dx}{x^4}\right] , \tag{4.33}$$

or, by using eq. (4.20),

$$<\Delta_{2,eff}>_c = \frac{1.42\varphi^2}{(1-1.42\varphi)}\eta_o G_{eff} . \tag{4.34}$$

Consequently, using the constraint $\eta_o G_o=\eta^\infty_{eff}G_{eff}$, we obtain the relation for the high frequency effective viscosity already presented in section 1, viz.

$$\eta^\infty_{eff} = \eta_o\left(1 + \frac{(\frac{5}{2}\varphi + 1.42\varphi^2)}{(1 - 1.42\varphi)}\right) . \tag{4.35}$$

Finally we express the stresslet $\overline{S}$ as a function of φ and G_o only, using eqs. (4.6) and (4.35),

$$\overline{S} = \tfrac{20}{3}\pi\eta_o a^3 \frac{1}{(1+1.08\varphi+1.42\varphi^2)} G_o \,. \tag{4.36}$$

The stresslet $\overline{S}$ is a function of volume fraction, although independent of particle configuration as assumed above eq. (4.8). This relation is an extension of an expression presented by Saito (ref. [9] eq. (8) with κ_o replaced by G_o and $\frac{20}{3}\pi\eta_o a^3<\kappa>$ replaced by $\overline{S}$). The numerical coefficient 1.08 arises from the subtraction $(\frac{5}{2} - 1.42)$ and in the Saito expression this coefficient is: $(\frac{5}{2} + c_S)=\frac{3}{2}$. The term of quadratic order in φ is an excluded volume effect and cannot be present in the Saito expression.

4.3 Discussion

In this section we shall compare our theoretical expression for the effective viscosity with experiment, other theories and results from simulation experiments and also discuss the limitations of our expression of η^{∞}_{eff}. We start with a remark on the divergent behaviour of our expression and the position of the pole, and see that our expression of the effective viscosity (eq. 4.35) has a pole near $\varphi\approx0.7$ which is something higher than $\varphi_{rc}\approx0.64$, the random close packing volume fraction. Furthermore it differs not much from the maximum packing fraction. There are arguments that we should compare our pole with φ_{rc}. One of these arguments is the fact that we used the isotropic pair distribution function while averageing over all possible particle configurations. In the case of maximum packed structures the isotropy has disappeared because there is some crystal–like structure. It is interesting to note that Krieger and Dougherty [29] introduced an empirical expression for η^{∞}_{eff}, later derived by Ball and Richmond using a mean field argument (see eqs. (6.4)–(6.6)

in ref. [30]),

$$\eta^{\infty}_{\text{eff}} = \eta_o(1-k_f\varphi)^{-(5/2k_f)}, \tag{4.37}$$

with k_f the reciprocal of the maximum packing fraction or the reciprocal of the random close packing fraction (Ball and Richmond). This expression is often used to fit experimental data with k_f as a fitting parameter (see e.g. ref. [31]).

In fig. 1 we have plotted the effective viscosity $\eta^{\infty}_{\text{eff}}$ as function of volume fraction. In this figure we compare our results of $\eta^{\infty}_{\text{eff}}$ with results of the effective viscosity of monodisperse hard sphere systems, experimentally obtained by van der Werff et al. [1]. We have made no distinction between the measurements on monodisperse systems with different particle radii because the data of van der Werff et al. do not show any effect of particle size. This can be expected on theoretical grounds. The theoretical result corresponds with the experimental data up to $\varphi \approx 0.6$. This is the more remarkable because we used two particle hydrodynamic interactions only to derive eq. (4.35). At the moment it is not clear how three and more particle hydrodynamic interactions will change our result of $\eta^{\infty}_{\text{eff}}$ but these interactions may shift the pole in eq. (4.35) to a slightly lower value (see the simulation results and numerical data discussed below). For reasons of completeness we have included in fig. 1 the theoretical results of Beenakker, derived by using many particle hydrodynamic interactions [12], and the virial expansion of Batchelor and Green, derived by using two particle hydrodynamic interactions only [5]. The analytical result of Batchelor and Green is

$$\eta^{\infty}_{\text{eff}} = \eta_o(1 + \tfrac{5}{2}\varphi + 5.2\varphi^2), \tag{4.38}$$

where they calculated the second order virial coefficient with an accuracy of 6%. More recent calculations, using more accurate hydrodynamic functions, give for the second order virial coefficient C_2=5.00 (see e.g. ref. [6] and [20]). We should obtain the same second order virial coefficient by expanding our result for small φ and the result is C_2=4.97. This

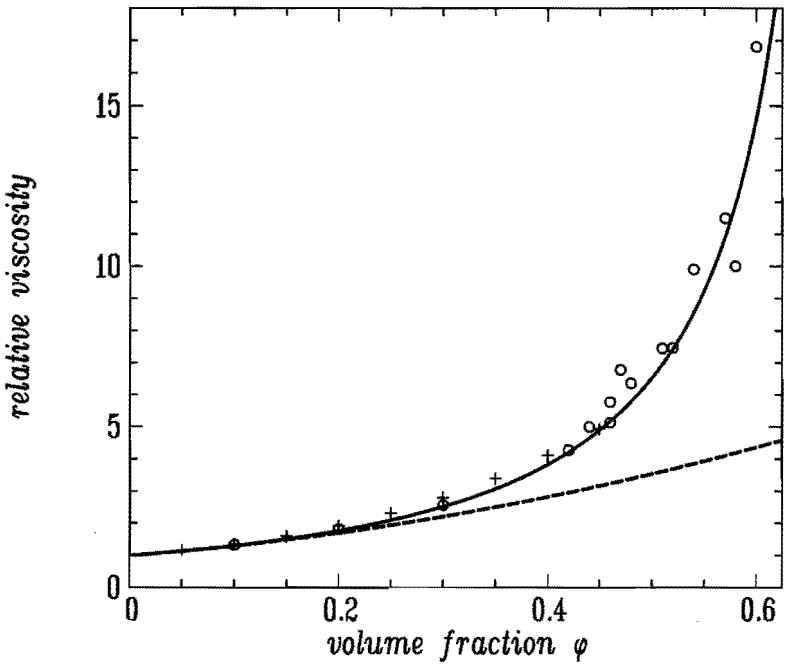

Fig.1. *The high frequency effective viscosity is plotted versus volume fraction φ. The solid curve represents our result, eq. (4.35), the dashed curve is the result of Batchelor and Green, eq. (4.38), and the plusses represent the theoretical results of Beenakker. The open circles are the experimental values of η^{∞}_{eff} obtained by van der Werff et al. for monodisperse hard sphere suspensions.*

difference may be caused by the fact that we have made the assumption of constant stresslets (see below eq. (4.7)) or by small numerical errors. Recently Thomas and Muthukumar presented results for the effective viscosity which include three particle hydrodynamic interactions [32]. Their expression is

$$\eta^{\infty}_{\text{eff}} = \eta_{\text{o}}(1 + \tfrac{5}{2}\varphi + 5.00\varphi^2 + 6.40\varphi^3)\,. \tag{4.39}$$

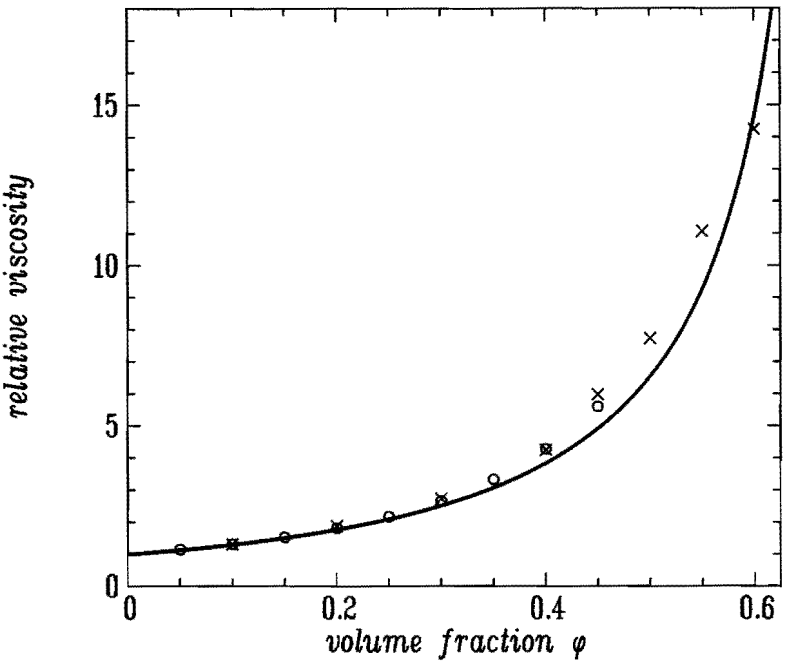

Fig.2. *The high frequency effective viscosity is plotted versus volume fraction φ. The solid curve represents our result, eq. (4.35). The crosses are the simulation results of Phillips et al. and the open circles are the numerical results of Ladd.*

This expression is a poor improvement that leads to the conclusion that many higher order terms should be included to obtain an expression that describes the experimental results and simulation data reasonably well. Nevertheless we can use the third order virial coefficient to make an estimate of the extra contribution to eq. (4.35), which is a combination of a pure three particle contribution and the two particle contribution, configurationally averaged with the φ dependent part of the pair distribution function. We assume that our expression should give the same cubic virial expansion in the low φ regime, but it is noteworthy to point out that this estimate gives an indication only. Supposing that $\epsilon\varphi^3$ is the combined three–two particle contribution, we obtain the following

expression:

$$\eta^{\infty}_{\text{eff}} = \eta_o\left(1 + \frac{\left(\frac{5}{2}\varphi + 1.42\varphi^2 - \epsilon\varphi^3\right)}{\left(1 - 1.42\varphi + \epsilon\varphi^2\right)}\right). \tag{4.40}$$

Low φ expansion using eq. (4.39) results in $\epsilon \approx 0.2$. There are some other estimates of the third order virial coefficient e.g. by using the Krieger–Dougherty relation (eq. 4.37)) or the Mooney equation [33], viz.

$$\eta^{\infty}_{\text{eff}} = \eta_o \exp\left[\frac{\frac{5}{2}\varphi}{(1-k_f\varphi)}\right] \tag{4.41}$$

with k_f a fitting parameter. The estimates made by Thomas and Muthukumar, based on the Krieger–Dougherty relation and the Mooney equation, give $C_3 \simeq 8.5$ [32]. In this case: $\epsilon \approx -0.4$. In both cases the three body coefficient ϵ is much smaller than the coefficient of the term representing two body effects, viz. 1.42. As such the use of a virial expansion in the numerator and in the denominator of eq. (4.40) converges much faster than the commonly used virial expansions of the viscosity itself. Future research should clarify this matter. The above discussion does not intend to question the importance of many particle hydrodynamic interactions, necessary to understand the behaviour of transport coefficients in dense suspensions. It tries to separate the effects of many particle hydrodynamic interactions from the divergence of the effective viscosity which is already found if one considers the lower order contributions to the viscosity.

In fig. 2 we have compared our theoretical result with simulation results of Phillips et al. [19] and with numerical data of Ladd [21] and we see that our theoretical result of $\eta^{\infty}_{\text{eff}}$ is systematically somewhat lower than the numerical data for $\varphi \gtrsim 0.4$. This difference may be explained by the fact that we have ignored many particle hydrodynamic interactions while both numerical results of $\eta^{\infty}_{\text{eff}}$ include the effect of many particle interactions. It is noteworthy to emphasize that our expression is not exact because we

have made the assumption of constant stresslets. Although our expression agrees very well with experimental results and numerical data it should be pointed out that an exact result is available, derived by Cichocki and Felderhof (see section 1 and ref. [11]). Finally we want to point out that Beenakker's remark about the range of validity of his theoretical results is also applicable to our results [12]. He derived a lower and an upper frequency limit and his results are valid between the two. The upper limit is determined by the frequency at which inertia effects become important. Below the lower frequency limit Brownian motion cannot be neglected. So our theoretical expression of the effective viscosity is thus valid between these limits. The data obtained by van der Werff et al. are results of measurements in this frequency range.

4.4 Conclusion

In this chapter we have derived an expression for the high frequency effective viscosity in a way similar to Saito's in the early fifties. The result is in good agreement with experimental data and the agreement with simulation results and numerical data is reasonable. It is known that many particle hydrodynamic interactions are, in general, important so higher order corrections to eq. (4.35) are to be studied, but these hydrodynamic interactions are likely to give small corrections to the expression derived in this chapter because the divergence in our expression for the effective viscosity is found if one considers two particle hydrodynamic interactions only. This is not the case if one considers the virial expansion (4.1), that results from the approach by Batchelor and Green [5]. This advantage should be exploited in future research. In the following chapter we shall present some results for diffusion coefficients and sedimentation (translational and rotational) where the effect of three particle interactions is included. The procedure presented in chapter 5, combined with the ideas outlined in this chapter, might give us the

answer to the question how eq. (4.35) should be corrected for three particle hydrodynamic interactions.

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Chapter 5 THREE PARTICLE HYDRODYNAMIC INTERACTIONS IN SUSPENSIONS

5.1 Introduction

In this chapter we present the results of a study of three particle hydrodynamic interactions and the effects of these interactions on diffusion and sedimentation. The three particle hydrodynamic interactions are studied by using the method to determine the grand mobility matrix of a system of N hydrodynamically interacting spherical particles, immersed in an unbounded fluid in the case N=3. In chapter 2 we have presented virial expansions of the translational and rotational self–diffusion coefficient and the sedimentation velocity, where two particle hydrodynamic interactions are included only. We are now able to determine the corrections of these virial expansions caused by three particle hydrodynamic interactions. The results in this article can be compared with theoretical results on the one hand and with numerical and experimental data on the other hand. Before we present the way of obtaining our results we give a brief historical sketch of the area of interest, which is not claimed to be complete.

Recent developments in both numerical and theoretical research on the behaviour of suspensions made it possible to improve the understanding of the transport and bulk properties of suspensions. In the area of numerical research progress has been made by the development of methods to simulate systems of Brownian particles, called Stokesian dynamics. With this method, developed by Brady and Bossis [1], it became possible to study transport coefficients, like e.g. translational and rotational self–diffusion coefficients, and bulk properties, like e.g. sedimentation and effective viscosity, numerically. Some interesting results of Stokesian dynamics simulation, which we shall use to compare our

results with, are presented in an article of Phillips, Brady and Bossis [2]. Many other authors have also presented results of simulation experiments on systems of Brownian particles to calculate transport coefficients of random hard sphere suspensions. Apart from this technique one can calculate these transport coefficients numerically and results of Ladd will be used in this case to compare our theoretical results with [3]. Apart from this numerical research great efforts have also been made with theoretical studies of systems of hard spheres in an ambient fluid under low Reynolds number conditions. Besides the hydrodynamic pair interactions between the spheres one has considered three and more particle hydrodynamic interactions. In the fifties Kynch used the reflection method to study hydrodynamic interactions between the particles of clusters of three and four spheres in a viscous fluid [4]. Some decades later, in the early eighties, Mazur and van Saarloos presented a general scheme to determine the components of the grand mobility matrix of a system of N spherical particles immersed in an unbounded fluid [5]. The expressions determined by those authors are power expansions in a/R, with a the particle radius and R typical interparticle distances. They derived explicit expressions for the components of the mobility matrix up to order R^{-7} and up to this order hydrodynamic interactions between two, three and four particles only contribute to these expressions. Beenakker has used the method of Mazur and van Saarloos to determine virial expansions of the short time self–diffusion coefficient, sedimentation and high frequency effective viscosity [6–8]. In the same articles he presented numerical results for the transport coefficients described above using an expansion in density fluctuation correlation functions. These results, taking into account many particle hydrodynamic interactions, correspond with experimental and simulation data very well. A disadvantage of these results is the fact that they are of numerical type instead of an expression in terms of e.g. volume fraction φ. In this way it is not possible to estimate the relative importance of two, three and more particle interactions respectively. For a concise summary we refer to a short review article of Mazur [9]. Felderhof [10] has given an outline how to proceed, using a method to study two

particle hydrodynamic interactions [11,12], to study the more general N particle problem. In another approach Cichocki and Felderhof presented a cluster expansion method to study the N particle problem, but, as far as we know, they used this method in the two–body approximation only [13]. Finally we want to emphasize the work of Muthukumar et al. In articles of Muthukumar and Freed a theory to study many particle hydrodynamic interactions is expounded [14,15]. Using this theory Jones, Muthukumar and Cohen were able to determine virial expansions of the cooperative and self friction coefficients [16]. We shall compare these expressions with some of our results.

In section 2 we present a reformulated set of linear equations appropriate for numerical purposes. We give the results of a study concerning the behaviour of some components of the grand mobility matrix, in the case of two special configurations of the three particle cluster, in section 3. A theoretical account of obtaining the virial expansions of some transport coefficients will be given in the sections 4 and 5 as well as the final results. We end the chapter with some concluding remarks.

5.2 Calculation of the mobility matrix

In chapter 2 we determined a set of linear equations (eqs. (2.36)–(2.38)) appropriate to describe the problem of N hydrodynamically interacting spherical particles, all with the same radius a, in a viscous fluid. We study this set of equations assuming N=3 and the fluid at rest at infinity. We have obtained this result by starting with an arbitrary configuration of the three particles but simplify it considerably by introducing a special coordinate system without affecting the generality of the set of linear equations. We number the particles and put particle 1 in the origin of a coordinate system, particle 2 on the negative z–axis and particle 3 in the xz–plane. Consequently we have: $\xi_{12}=0$, $\eta_{13}=\pi$ and $\eta_{23}=\pi$. Furthermore we use the relations $\xi_{ji}=\pi-\xi_{ij}$ and $\eta_{ji}=\eta_{ij}+\pi$. This procedure is in

principle equivalent to the one used in chapter 3, where we have put both particles on the z–axis to describe two particle hydrodynamic interactions. In that special case we were able to decouple the set of linear equations with respect to the azimuthal indices. This simplification is of course not possible in the three particle case. An exception should be made if the third particle is also on the z–axis. Introduce furthermore the new coefficients $\{A^{\pm i}_{lm}, B^{\pm i}_{lm}, C^{\pm i}_{lm}\}$,

$$\text{(5.1a)} \quad A^{\pm i}_{lm} = \frac{(-1)^{l+m}}{n_{lm} a^{l+2}} (\alpha^{i}_{lm} \pm (-1)^{m} \alpha^{i}_{l,-m}) , \quad A^{\pm i}_{l,-m} = \pm (-1)^{m} \frac{(l+m)!}{(l-m)!} A^{\pm i}_{lm} ,$$

$$\text{(5.1b)} \quad B^{\pm i}_{lm} = -i \frac{(-1)^{l+m}}{n_{lm} a^{l+1}} (\beta^{i}_{lm} \pm (-1)^{m} \beta^{i}_{l,-m}) , \quad B^{\pm i}_{l,-m} = \pm (-1)^{m} \frac{(l+m)!}{(l-m)!} B^{\pm i}_{lm} ,$$

$$\text{(5.1c)} \quad C^{\pm i}_{lm} = \frac{(-1)^{l+m}}{n_{lm} a^{l}} (\gamma^{i}_{lm} \pm (-1)^{m} \gamma^{i}_{l,-m}) , \quad C^{\pm i}_{l,-m} = \pm (-1)^{m} \frac{(l+m)!}{(l-m)!} C^{\pm i}_{lm} .$$

We see from these relations that it is sufficient to use the plus coefficients, A^{+i}_{lm} etc., with $m \geq 0$ and the minus coefficients, A^{-i}_{lm} etc., with $m > 0$ only. With this new set of coefficients we are able to derive two simplified sets of linear equations, which are independent of each other. With one set we can study the components of the grand mobility matrix relating translations of the particles in the z– and x–direction and rotations of the particles in the y–direction, on the one hand, with the forces exerted by the fluid on the particles in the z– and x–direction and the torques exerted on the particles in the y–direction, on the other hand. In the other set the role of translations and rotations is interchanged as is the case with the forces and torques. We do not present the total derivation of the rewritten set of linear equations but the final result only, which comes to:

$$(5.2)\qquad \frac{(-1)^{p+q}}{p(p+1)n_{pq}}\int_{|\underline{r}_i|=a}\underline{v}^{i}(\underline{r}_i)\cdot(\underline{A}^{*}_{pq}(\theta_i,\varphi_i)+(-1)^{q}\underline{A}^{*}_{p,-q}(\theta_i,\varphi_i))\mathrm{d}\Omega_i$$

$$=-\tfrac{3}{2}\delta_{p,1}\left[\delta_{q,1}U_{ix}+2\delta_{q,0}U_{iz}\right]$$

$$=C^{+i}_{pq}+\sum_{\substack{j=1\\ j\neq i}}^{3}\left[\frac{(2p+1)}{(p+1)}\sum_{\substack{l\geq 1\\ m\geq 0}}\frac{l}{(l+1)(2l+1)}P^{+ji}_{lm;pq}x^{l+p+1}_{ij}A^{+j}_{lm}+\frac{(2p+1)}{p(p+1)}\sum_{\substack{l\geq 1\\ m\geq 1}}\frac{1}{l(l+1)}Q^{-ji}_{lm;pq}x^{l+p}_{ij}B^{-j}_{lm}\right.$$

$$+\frac{1}{2(p+1)}\sum_{\substack{l\geq 1\\ m\geq 0}}l(2l-1)P^{+ji}_{lm;pq}x^{l+p+1}_{ij}C^{+j}_{lm}-\frac{(2p+1)}{2(p+1)}\sum_{\substack{l\geq 1\\ m\geq 0}}\frac{l(2l-1)}{(2l+2p-1)}P^{+ji}_{lm;pq}x^{l+p-1}_{ij}C^{+j}_{lm}$$

$$\left.+\frac{(2p+1)}{p(p+1)(2p-1)}\sum_{\substack{l\geq 1\\ m\geq 0}}\frac{2l+2p-lp-1}{(2l+2p-1)}R^{+ji}_{lm;pq}x^{l+p-1}_{ij}C^{+j}_{lm}\right],$$

$$(5.3)\qquad A^{+i}_{pq}=\tfrac{1}{2}(p+1)(2p-1)C^{+i}_{pq}-\frac{1}{2p+3}\sum_{\substack{j=1\\ j\neq i}}^{3}\sum_{\substack{l\geq 1\\ m\geq 0}}l(2l-1)P^{+ji}_{lm;pq}x^{l+p+1}_{ij}C^{+j}_{lm},$$

$$(5.4)\qquad i\frac{(-1)^{p+q+1}}{n_{pq}}\int_{|\underline{r}_i|=a}\underline{v}^{i}(\underline{r}_i)\cdot(\underline{C}^{*}_{pq}(\theta_i,\varphi_i)-(-1)^{q}\underline{C}^{*}_{p,-q}(\theta_i,\varphi_i))\mathrm{d}\Omega_i=2a\delta_{p,1}\delta_{q,1}\Omega_{iy}$$

$$=B^{-i}_{pq}-\sum_{\substack{j=1\\ j\neq i}}^{3}\left[p\sum_{\substack{l\geq 1\\ m\geq 1}}\frac{1}{(l+1)}P^{-ji}_{lm;pq}x^{l+p+1}_{ij}B^{-j}_{lm}+\sum_{\substack{l\geq 1\\ m\geq 0}}(2l-1)Q^{+ji}_{lm;pq}x^{l+p}_{ij}C^{+j}_{lm}\right].$$

In the derivation of these equations, which can be done straightforwardly, we have used eqs. (2.44), (2.45) and (2.48) with the assumption of zero surface averaged incoming fluid velocity and vorticity. Furthermore we have introduced the following shorthand notations:

$$(5.5)\qquad P^{\pm ji}_{lm;pq}=\frac{(-1)^{l+p+m+q}}{(p+q)!}n_{lm}R^{l+p+1}_{ij}\left[M^{ji}_{lm;pq}\pm(-1)^{m}M^{ji}_{l,-m;pq}\right]$$

$$(5.6)\qquad Q^{\pm\,ji}_{lm;pq} = \frac{(-1)^{l+p+m+q}}{(p+q)\,!}\, n_{lm} R^{l+p}_{ij}\Big[(lq+mp)M^{ji}_{lm;p-1,q} \pm (-1)^m (lq-mp) M^{ji}_{l,-m;p-1,q}\Big]$$

$$(5.7)\qquad R^{\pm\,ji}_{lm;pq} = \frac{(-1)^{l+p+m+q}}{(p+q)\,!}\, n_{lm} R^{l+p-1}_{ij}\Big[\Big[(lq+mp)[2(lq+mp)-(m+q)] - (lp+mq)(l+p-1)\Big] M^{ji}_{lm;p-2,q} \pm (-1)^m \Big[(lq-mp)[2(lq-mp)+(m-q)] - (lp-mq)(l+p-1)\Big] M^{ji}_{l,-m;p-2,q}\Big]$$

It is possible to solve the set of linear equations (5.2)–(5.4) partially if we express all coefficients A^{+i}_{lm}, with $l \geq 1$, B^{-i}_{lm}, with $l \geq 2$, and C^{+i}_{lm}, with $l \geq 2$, for $i \in \{1,2,3\}$, in terms of the coefficients B^{-i}_{11}, C^{+i}_{10} and C^{+i}_{11}. This procedure resembles the one used in chapter 3. We can express the remaining coefficients in terms of components of the force $\underline{F}_i$ and torque $\underline{T}_i$ by using eqs. (2.53) and (2.54),

$$(5.8)\qquad B^{-i}_{11} = -\frac{1}{4\pi\eta_o a^2} T_{iy}\,, \quad C^{+i}_{10} = \frac{1}{2\pi\eta_o a} F_{iz}\,, \quad C^{+i}_{11} = \frac{1}{4\pi\eta_o a} F_{ix}\,.$$

Finally we obtain the following relation between $\underline{U}_x$, $\underline{U}_z$ and $\underline{\Omega}_y$ on the one hand and $\underline{F}_x$, $\underline{F}_z$ and $\underline{T}_y$ on the other hand, with $\underline{U}_x = (U_{1x}, U_{2x}, U_{3x})$ etc.:

$$(5.9)\qquad \begin{bmatrix} \underline{U}_x \\ \underline{U}_z \\ \underline{\Omega}_y \end{bmatrix} = -\begin{bmatrix} \mu^{tt}_{xx} & \mu^{tt}_{xz} & \mu^{tr}_{xy} \\ \mu^{tt}_{zx} & \mu^{tt}_{zz} & \mu^{tr}_{zy} \\ \mu^{rt}_{yx} & \mu^{rt}_{yz} & \mu^{rr}_{yy} \end{bmatrix} \cdot \begin{bmatrix} \underline{F}_x \\ \underline{F}_z \\ \underline{T}_y \end{bmatrix}.$$

In an analogous way, using the shorthand notations defined above (eqs. (5.5)–(5.7)), we obtain

$$(5.10)\qquad \frac{(-1)^{p+q}}{p(p+1)n_{pq}}\int_{|\underline{r}_i|=a}\underline{v}^{i}(\underline{r}_i)\cdot(\underline{A}^{*}_{pq}(\theta_i,\varphi_i)-(-1)^{q}\underline{A}^{*}_{p,-q}(\theta_i,\varphi_i))\mathrm{d}\Omega_i=\tfrac{3}{2}i\delta_{p,1}\delta_{q,1}U_{iy}$$

$$=C^{-i}_{pq}+\sum_{\substack{j=1\\ j\neq i}}^{3}\Bigg[\frac{(2p+1)}{(p+1)}\sum_{\substack{l\geq 1\\ m\geq 1}}\frac{l}{(l+1)(2l+1)}P^{-ji}_{lm;pq}x_{ij}^{l+p+1}A^{-j}_{lm}+\frac{(2p+1)}{p(p+1)}\sum_{\substack{l\geq 1\\ m\geq 0}}\frac{1}{l(l+1)}Q^{+ji}_{lm;pq}x_{ij}^{l+p}B^{+j}_{lm}$$

$$+\frac{1}{2(p+1)}\sum_{\substack{l\geq 1\\ m\geq 1}}l(2l-1)P^{ji}_{lm;pq}x_{ij}^{l+p+1}C^{-j}_{lm}-\frac{(2p+1)}{2(p+1)}\sum_{\substack{l\geq 1\\ m\geq 1}}\frac{l(2l-1)}{(2l+2p-1)}P^{-ji}_{lm;pq}x_{ij}^{l+p-1}C^{-j}_{lm}$$

$$+\frac{(2p+1)}{p(p+1)(2p-1)}\sum_{\substack{l\geq 1\\ m\geq 1}}\frac{2l+2p-lp-1}{(2l+2p-1)}R^{-ji}_{lm;pq}x_{ij}^{l+p-1}C^{-j}_{lm}\Bigg],$$

$$(5.11)\qquad A^{-i}_{pq}=\tfrac{1}{2}(p+1)(2p-1)C^{-i}_{pq}-\frac{1}{2p+3}\sum_{\substack{j=1\\ j\neq i}}^{3}\sum_{\substack{l\geq 1\\ m\geq 1}}l(2l-1)P^{-ji}_{lm;pq}x_{ij}^{l+p+1}C^{-j}_{lm},$$

$$(5.12)\qquad i\frac{(-1)^{p+q+1}}{n_{pq}}\int_{|\underline{r}_i|=a}\underline{v}^{i}(\underline{r}_i)\cdot(\underline{C}^{*}_{pq}(\theta_i,\varphi_i)+(-1)^{q}\underline{C}^{*}_{p,-q}(\theta_i,\varphi_i))\mathrm{d}\Omega_i$$

$$=2ia\delta_{p,1}\left[\delta_{q,1}\Omega_{ix}+2\delta_{q,0}\Omega_{iz}\right]$$

$$=B^{+i}_{pq}-\sum_{\substack{j=1\\ j\neq i}}^{3}\Bigg[p\sum_{\substack{l\geq 1\\ m\geq 0}}\frac{1}{(l+1)}P^{+ji}_{lm;pq}x_{ij}^{l+p+1}B^{+j}_{lm}+\sum_{\substack{l\geq 1\\ m\geq 1}}(2l-1)Q^{-ji}_{lm;pq}x_{ij}^{l+p}C^{-j}_{lm}\Bigg].$$

In the way described above we are able to solve partially this set of linear equations. Using the relations

$$(5.13) \qquad B_{10}^{+i} = -\frac{i}{2\pi\eta_o a^2} T_{iz}\,, \quad B_{11}^{+i} = -\frac{i}{4\pi\eta_o a^2} T_{ix}\,, \quad C_{11}^{-i} = -\frac{i}{4\pi\eta_o a} F_{iy}\,,$$

we can present the final result in the following form:

$$(5.14) \qquad \begin{bmatrix} \underline{\Omega}_x \\ \underline{\Omega}_z \\ \underline{U}_y \end{bmatrix} = -\begin{bmatrix} \mu_{xx}^{rr} & \mu_{xz}^{rr} & \mu_{xy}^{rt} \\ \mu_{zx}^{rr} & \mu_{zz}^{rr} & \mu_{zy}^{rt} \\ \mu_{yx}^{tr} & \mu_{yz}^{tr} & \mu_{yy}^{tt} \end{bmatrix} \cdot \begin{bmatrix} \underline{T}_x \\ \underline{T}_z \\ \underline{F}_y \end{bmatrix} .$$

We have made a computer programme in Fortran–77 to calculate the components of the grand mobility matrix (represented by eqs. (5.9) and (5.14)) for arbitrary particle configurations. This computer programme is obtainable from the authors upon request.

5.3 Two special configurations

We shall now present the results of a study of the behaviour of some components of the grand mobility matrix in the case of two special configurations. In the first configuration we put the three particles on the z–axis of a coordinate system with origin at the center of particle 1. Particle 2 is placed between the two other particles. This is a suitable configuration because there are some numerical results available to compare our results with [17]. In the second configuration we put the three particles on the corners of an equilateral triangel. This configuration has the property that the three particles can touch each other simultaneously. There are many other configurations possible which are suitable to study, e.g. configurations with a very pronounced three particle contribution to the components of the grand mobility matrix. However, we have to restrict ourselves and therefore we pay attention to the two symmetric configurations described above only.

We consider now the first configuration with

$$(5.15) \qquad |\underline{R}_{13}|=2|\underline{R}_{12}| \ , \ |\underline{R}_{12}|=|\underline{R}_{23}| \ ; \ \xi_{12}=0 \ , \ \xi_{13}=0 \ , \ \xi_{23}=0 \ .$$

Use of eq. (5.15) in the set of linear equations results in a decoupling of this set concerning the azimuthal indices (see eq. (2.33)). This decoupling procedure is comparable to the one used in chapter 3. We use it to simplify the computer programme, necessary to solve the set of linear equations, considerably. The set of linear equations solved allows us to determine the components of the grand mobility matrix. Formally we have an infinite set of linear equations. We can avoid the problem of solving an infinite set of linear equations by introducing an upper limit for the allowed values of l and p, i.e. $l_{max}=p_{max}=L$. With this upper limit it is possible to solve the set of linear equations. This restriction is nothing but the assumption that all the coefficients $A^{\pm i}_{lm}$, $B^{\pm i}_{lm}$ and $C^{\pm i}_{lm}$ are zero for $l>L$. With the upper limit L we have $9L$ linear equations with the same number of unknown coefficients and can calculate the so called L^{th} order solution of the set of linear equations. In the present problem we confine ourselves to the presentation of the components of the mobility matrices μ^{tt}_{zz} and μ^{rr}_{zz}. Using symmetry arguments we see that $\mu^{tt}_{zx}=0$, $\mu^{tr}_{zy}=0$, $\mu^{rr}_{zx}=0$ and $\mu^{rt}_{zy}=0$ (more mobility matrices are zero in this special case but they are of no significance to us). Using eqs. (5.9) and (5.14) we obtain respectively

$$(5.16) \qquad \underline{U}_z = -\mu^{tt}_{zz}\cdot\underline{F}_z \ , \quad \underline{\Omega}_z = -\mu^{rr}_{zz}\cdot\underline{T}_z$$

where we used the shorthand notations $\underline{U}_z=(U_{1z},U_{2z},U_{3z})$ etc. We present our results in table I. The rows labeled with $L=\infty$ represent limiting values of the components of the mobility matrix resulting from our method. We also give the results obtained by Ladd [17]. We have used his limiting results only; he obtained them by a numerical implementation of the work of Mazur and van Saarloos [5]. In this table: $\bar{\mu}^{tt}_{ij,zz} \equiv 6\pi\eta_o a\mu^{tt}_{ij,zz}$. We can conclude

TABLE I

P3: *pure three particle contribution*
∞: *limiting values obtained by our method*
Ladd: *results obtained by Ladd [17]*
PE: *contribution according to eqs. (5.18)*

a/R_{12}	L	$\bar{\mu}^{tt}_{11,zz}$	P3	$\bar{\mu}^{tt}_{22,zz}$	P3	$\bar{\mu}^{tt}_{12,zz}$	$\bar{\mu}^{tt}_{13,zz}$
0.50	2	0.85835	−0.03215	0.83045	0.02550	0.59764	0.48574
	4	0.77368	−0.05764	0.74480	0.05572	0.62193	0.53935
	6	0.73473	−0.07283	0.70957	0.06800	0.63168	0.57253
	10	0.69797	−0.08893	0.68081	0.08057	0.63962	0.60479
	20	0.66855	−0.10299	0.66088	0.09135	0.64531	0.63095
	50	0.65341	−0.11062	0.65150	0.09698	0.64799	0.64457
	100	0.65012	−0.11232	0.64955	0.09821	0.64854	0.64754
	Ladd	0.7459		0.7182		0.6292	0.5628
	PE		−0.07324		0.03662		
0.48	2	0.87251	−0.02721	0.84181	0.02171	0.58420	0.46059
	4	0.80323	−0.04544	0.76561	0.04562	0.60569	0.50060
	6	0.77649	−0.05441	0.73781	0.05335	0.61363	0.52256
	10	0.75871	−0.06087	0.72055	0.05873	0.61844	0.53757
	20	0.75442	−0.06246	0.71651	0.06012	0.61961	0.54117
	∞	0.75438	−0.06247	0.71649	0.06013	0.61962	0.54120
	PE		−0.05504		0.02752		
0.45	2	0.89426	−0.01998	0.86088	0.01608	0.56217	0.42167
	4	0.84857	−0.02868	0.80238	0.03019	0.57818	0.44217
	6	0.83807	−0.03101	0.78808	0.03219	0.58248	0.45001
	10	0.83506	−0.03168	0.78383	0.03262	0.58364	0.45231
	∞	0.83494	−0.03171	0.78365	0.03264	0.58370	0.45240
	PE		−0.03503		0.01752		
0.40	2	0.92777	−0.01036	0.89514	0.00833	0.52027	0.35783
	4	0.90765	−0.01187	0.86301	0.01272	0.52799	0.36064
	6	0.90597	−0.01194	0.85973	0.01266	0.52910	0.36157
	∞	0.90581	−0.01195	0.85939	0.01262	0.52919	0.36167
	PE		−0.01536		0.00768		
0.25	2	0.98667	−0.00049	0.97638	0.00033	0.35620	0.19793
	4	0.98542	−0.00047	0.97393	0.00037	0.35630	0.19705
	∞	0.98541	−0.00047	0.97391	0.00037	0.35631	0.19704
	Ladd	0.9854		0.9739		0.3563	0.1971
	PE		−0.00057		0.00029		
0.125	2	0.99907	−0.00000	0.99826	0.00000	0.18533	0.09438
	∞	0.99904	−0.00000	0.99821	0.00000	0.18532	0.09436
	Ladd	0.9991		0.9983		0.1853	0.0944

that there are differences between our results and those of Ladd in the case of touching spheres, $|\underline{R}_{12}|=2a$. The origin of this difference is the fact that Ladd used a low order moment approximation to determine his results. In that case it is necessary to evaluate the calculations with large L in order to obtain reasonable results (in our case up to L=100). Furthermore we can conclude that, if $|\underline{R}_{12}|=2a$, the components of μ_{zz}^{tt} tend to the same value, which we denote by α, and

$$U_{iz} = -\alpha \sum_{j=1}^{3} F_{jz} \quad , i\in\{1,2,3\} , \tag{5.17}$$

where $\alpha\approx 0.649$. This approximate value is obtained by considering the numerical data up to L=100 and by assuming that the components of μ_{zz}^{tt} should be equal, which will be argued below. This leads to an upper and lower limit for α, $0.64854<\alpha<0.64955$. In the two particle problem we can see the same situation as in the case of μ_{zz}^{tt}, with $\alpha\approx 0.7750$ (see e.g. ref. [18], and our results in chapter 3). This can be explained as follows: if a force F, in the z–direction, is exerted on particle 1 that particle will translate with velocity U, in the z–direction too, but the second particle will also translate with this velocity U. This behaviour is easy to understand if the force on particle 1 is in the direction of particle 2 because the touching particles are supposed to be hard spheres. That we find the same behaviour if the force is in the opposite direction, is a direct consequence of the stick boundary conditions (eq. (2.3)). If the first particle tends to move away a large fluid velocity difference arises in a small region of space between the surfaces of the two particles [18]. This difference can be cancelled if the second particle translates with the first. The three particle case described above can be explained in the same way, but it is also necessary to use the symmetry relations for the mobility matrix μ_{zz}^{tt} (eq. (2.13)) to understand the equivalence of the three particles although the outer particles see a different environment in comparison to the particle between them. The results in table I in the columns labelled with P3 represent the contribution of pure three particle hydrodynamic

interactions to $\mu^{tt}_{11,zz}$ and $\mu^{tt}_{22,zz}$. From these results we see that three particle interactions are important, especially for small interparticle distances, and that the convergence behaviour is slow. Finally in tabel I, in the row denoted by PE, we have presented the pure three particle contributions obtained from the first term of the power expansion in inverse interparticle distances, which has the following form [5]:

$$(5.18a)\quad 6\pi\eta_o a\mu^{tt}_{11,zz} = -\tfrac{75}{8}\, x_{12}^2 x_{13}^2 x_{23}^3\, \zeta_1((1-3\zeta_2^2)(1-3\zeta_3^2)+6\zeta_2^2\zeta_3^2+6\zeta_1\zeta_2\zeta_3) = -\tfrac{75}{8}\, x_{12}^7\,,$$

$$(5.18b)\quad 6\pi\eta_o a\mu^{tt}_{22,zz} = -\tfrac{75}{8}\, x_{12}^2 x_{13}^3 x_{23}^2\, \zeta_2((1-3\zeta_1^2)(1-3\zeta_3^2)+6\zeta_1^2\zeta_3^2+6\zeta_1\zeta_2\zeta_3) = \tfrac{75}{16}\, x_{12}^7\,,$$

for $\mu^{tt}_{11,zz}$ and $\mu^{tt}_{22,zz}$ respectively. The last expression in both equations is the result for the special configuration described above. Furthermore: $\zeta_1=\cos\xi_{13}$, $\zeta_2=-\cos\xi_{23}$ and $\zeta_3=\cos(\xi_{23}-\xi_{13})$. We can see that the pure three particle contributions, determined with our method, differ significantly from the results from eqs. (5.18a) and (5.18b). It is obvious that these relations cannot be used to describe three particle interactions very satisfactorily, even at intermediate interparticle distances. We have also studied the numerical data of μ^{tt} for large interparticle distances and the conclusion is that relations like eqs. (5.18a) and (5.18b) are valid only if the three interparticle distances are simultaneously large. There are especially different results for the pure three particle contributions, and convergence problems, if e.g. $|\underline{R}_{12}|>>2a$, $|\underline{R}_{13}|>>2a$ but $|\underline{R}_{23}|\approx 2a$. This behaviour forces us to be cautious in the case of numerical calculations like e.g. the calculation of configuration averages as we shall see in the next section. We have also studied the behaviour of $\mu^{rr}_{ij,zz}$; the results are presented in table II. To our knowledge there are no results available to compare them with. The convergence behaviour of the $\mu^{rr}_{ij,zz}$ is considerably faster than the convergence behaviour of the translational counterpart described in table I. The same is true if we consider the pure three particle contributions. This kind of convergence behaviour has also been shown in the two particle case (ch. 3).

TABLE II

P3: *pure three particle contribution*
∞: *limiting values obtained by our method*

a/R_{12}	L	$\bar{\mu}^{rr}_{11,zz}$	P3	$\bar{\mu}^{rr}_{22,zz}$	P3	$\bar{\mu}^{rr}_{12,zz}$	$\bar{\mu}^{rr}_{13,zz}$
0.50	2	0.98767	−0.00038	0.97665	0.00046	0.12427	0.02791
	4	0.97734	−0.00049	0.95721	0.00146	0.12830	0.02594
	6	0.97404	−0.00048	0.95082	0.00167	0.13110	0.02597
	10	0.97182	−0.00048	0.94635	0.00164	0.13314	0.02632
	20	0.97057	−0.00050	0.94388	0.00165	0.13425	0.02659
	50	0.97011	−0.00050	0.94301	0.00168	0.13464	0.02669
	100	0.97003	−0.00051	0.94286	0.00169	0.13470	0.02671
0.48	2	0.99122	−0.00020	0.98315	0.00023	0.11006	0.02257
	4	0.98510	−0.00022	0.97129	0.00058	0.11203	0.02074
	6	0.98392	−0.00020	0.96889	0.00058	0.11299	0.02053
	10	0.98361	−0.00019	0.96815	0.00053	0.11332	0.02053
	∞	0.98358	−0.00019	0.96814	0.00052	0.11334	0.02053
0.45	2	0.99483	−0.00008	0.98993	0.00008	0.09081	0.01654
	4	0.99194	−0.00007	0.98423	0.00016	0.09146	0.01533
	6	0.99161	−0.00007	0.98355	0.00015	0.09167	0.01520
	∞	0.99157	−0.00006	0.98346	0.00014	0.09171	0.01519
0.40	2	0.99801	−0.00001	0.99607	0.00001	0.06388	0.00998
	4	0.99720	−0.00001	0.99446	0.00002	0.06396	0.00954
	∞	0.99715	−0.00001	0.99435	0.00002	0.06398	0.00951
0.25	2	0.99995	−0.00000	0.99991	0.00000	0.01562	0.00200
	∞	0.99995	−0.00000	0.99990	0.00000	0.01562	0.00199

We now consider a more complicated problem with the third particle in the xz–plane. The decoupling of the set of linear equations disappears and it becomes more difficult to solve the set of linear equations for large L. In the case described above we had to solve $9L$ linear equations but in general one has to solve $9L(L+2)$ linear equations. It will be obvious that the number of linear equations to be solved increases sharply with the increase of L. Consequently we have a numerical upper limit for L itself. Despite this limitation, we are able to study the general problem reasonably well. Suppose the following situation:

$$|\underline{R}_{12}|=|\underline{R}_{13}|=|\underline{R}_{23}| \; ; \; \xi_{12}=0 \, , \; \xi_{13}=\tfrac{1}{3}\pi \, , \; \xi_{23}=\tfrac{2}{3}\pi \, . \tag{5.19}$$

In table III and IV we present the results of $\mu^{tt}_{11,\alpha\alpha}$ and $\mu^{rr}_{11,\alpha\alpha}$ respectively, with $\alpha\in\{x,y,z\}$, for several values of $|\underline{R}_{12}|$. It is not necessary to study the components of the mobility matrices μ^{tt} and μ^{rr} for i=2 or 3, because they are related to those presented in both tables. The values in the columns labelled with P3 are again the pure three particle contributions, the rows labelled with $L=\infty$ represent limiting results obtained by our method and the values in the rows denoted by PE are determined with eq. (5.18a). This expression gives, in our special configuration, results for the $\mu^{tt}_{11,zz}$ only because the relations describing the three particle contribution to $\mu^{tt}_{11,xx}$ and $\mu^{tt}_{11,yy}$ are expressed in terms of typical inverse interparticle distances of order R^{-9} and higher. The conclusion here is that three particle hydrodynamic interactions cannot be accounted for by a single term. This becomes especially clear if we consider nearly touching spheres. Mazur and van Saarloos have presented some expressions for μ^{tt}_{ij} and μ^{rr}_{ij} [5]. These expressions have the following inverse interparticle distance dependence, with R representing the interparticle distances, all equal in the present case:

$$\mu^{tt}_{ii,xx} = O(R^{-9}) \,,\quad \mu^{tt}_{ii,yy} = O(R^{-9}) \,,\quad \mu^{tt}_{ii,zz} = O(R^{-7}) \,, \tag{5.20}$$

$$\mu^{rr}_{ii,\alpha\alpha} = O(R^{-8}) \,,\ \alpha\in\{x,y,z\} \,. \tag{5.21}$$

This behaviour is not present in the tables III and IV, as we may expect, keeping in mind the same kind of problems in the two particle case. So it is obvious that we have to take into account many more terms of the power expansion in inverse interparticle distances. It should be noted that our method gives results which are not expressed in terms of power expansions. See in this context the discussion in the chapters 2 and 3. It is remarkable that for nearly touching spheres the rotational mobilities are more influenced by the pure three particle hydrodynamic interactions than the translational mobilities. In this context we want to point out that it could be interesting to work out these three particle problems by

TABLE III

P3: *pure three particle contribution*
∞: *limiting values obtained by our method*
PE: *contribution according to eqs. (5.18)*

a/R_{12}	L	$\bar{\mu}^{tt}_{11,xx}$	P3	$\bar{\mu}^{tt}_{11,yy}$	P3	$\bar{\mu}^{tt}_{11,zz}$	P3
0.50	2	0.90037	0.00648	0.95015	0.00288	0.85997	0.00166
	4	0.84875	0.01425	0.92859	0.00682	0.78309	0.00675
	6	0.82770	0.01919	0.91694	0.00828	0.75298	0.01125
	10	0.80605	0.02238	0.90454	0.01081	0.72329	0.01299
	15	0.79559	0.02588	0.89658	0.01270	0.70854	0.01494
	PE						−0.04349
0.48	2	0.91302	0.00492	0.96258	0.00167	0.87316	0.00025
	4	0.87009	0.00744	0.95083	0.00258	0.80671	0.00113
	6	0.85525	0.00795	0.94741	0.00242	0.78459	0.00243
	10	0.84470	0.00686	0.94577	0.00232	0.76892	0.00149
	15	0.84271	0.00682	0.94555	0.00230	0.76587	0.00156
	PE						−0.03268
0.45	2	0.92947	0.00309	0.97605	0.00071	0.89280	−0.00095
	4	0.89899	0.00294	0.97107	0.00069	0.84430	−0.00221
	6	0.89228	0.00268	0.97039	0.00057	0.83412	−0.00199
	10	0.89008	0.00233	0.97023	0.00054	0.83076	−0.00238
	∞	0.89001	0.00233	0.97022	0.00054	0.83063	−0.00238
	PE						−0.02080
0.40	2	0.95198	0.00124	0.98925	0.00015	0.92376	−0.00141
	4	0.93689	0.00064	0.98793	0.00010	0.89913	−0.00273
	6	0.93557	0.00055	0.98788	0.00008	0.89714	−0.00270
	∞	0.93543	0.00052	0.98787	0.00008	0.89691	−0.00274
	PE						−0.00912
0.25	2	0.99074	0.00002	0.99951	0.00000	0.98466	−0.00019
	4	0.98973	0.00000	0.99943	0.00000	0.98301	−0.00025
	∞	0.98972	0.00000	0.99943	0.00000	0.98300	−0.00025
	PE						−0.00034

using algabraic computer programmes. The final expressions of the components of the grand mobility matrix are then expressed as a fraction with both the numerator and the denominator described in terms of spherical harmonics and inverse typical interparticle distances.

Finally we want to discuss some results for sedimentation of this system of particles with the special configuration introduced above. Durlofsky, Brady and Bossis [19] have

TABLE IV

P3: *pure three particle contribution*
∞: *limiting values obtained by our method*

a/R_{12}	L	$\bar{\mu}^{rr}_{11,xx}$	P3	$\bar{\mu}^{rr}_{11,yy}$	P3	$\bar{\mu}^{rr}_{11,zz}$	P3
0.50	2	0.91508	0.00524	0.88093	0.01090	0.93872	0.00234
	4	0.81660	0.01477	0.74133	0.03185	0.86567	0.00227
	6	0.76750	0.02228	0.68414	0.06128	0.82972	0.00293
	10	0.71639	0.03427	0.60853	0.08396	0.78731	0.00016
	15	0.68213	0.04451	0.56113	0.10671	0.75835	−0.00140
0.48	2	0.93408	0.00311	0.90936	0.00956	0.95342	0.00167
	4	0.86910	0.00618	0.82760	0.02937	0.90857	0.00254
	6	0.84631	0.00786	0.80102	0.04049	0.89320	0.00280
	10	0.83320	0.00944	0.78210	0.04468	0.88406	0.00274
	15	0.83063	0.00988	0.77823	0.04560	0.88229	0.00279
0.45	2	0.95570	0.00131	0.94005	0.00693	0.96950	0.00092
	4	0.92074	0.00148	0.89877	0.01840	0.94658	0.00139
	6	0.91315	0.00162	0.88867	0.02026	0.94163	0.00135
	10	0.91112	0.00169	0.88557	0.02047	0.94032	0.00133
	∞	0.91104	0.00170	0.88543	0.02048	0.94026	0.00133
0.40	2	0.97852	−0.00022	0.97091	0.00326	0.98569	0.00029
	4	0.96684	−0.00002	0.95687	0.00656	0.97829	0.00039
	6	0.96569	−0.00002	0.95504	0.00650	0.97754	0.00038
	∞	0.96559	−0.00002	0.95486	0.00649	0.97747	0.00037
0.25	2	0.99880	−0.00000	0.99821	0.00008	0.99925	0.00000
	∞	0.99860	−0.00001	0.99793	0.00010	0.99912	0.00000

discussed this problem, using also some unpublished results of Kim (1985). We consider sedimentation of this three particle cluster in the y–direction, being the configuration appropriate to compare our results with those of Durlofsky et al. We are interested in the drag coefficient λ which is defined as follows:

$$\lambda = (\mu^{tt}_{11,yy}+\mu^{tt}_{12,yy}+\mu^{tt}_{13,yy})^{-1} \tag{5.22}$$

Kim was able to study the coefficient λ up to x=a/R=0.4. At smaller interparticle spacings the convergence behaviour of his power expansion is very slow. Kim used extrapolated

values for smaller interparticle spacings [20,19]. We were able to study λ up to x=0.5 and the results resemble those of Durlofsky et al., but it seems that at very small interparticle spacings our results are slightly lower than those of Durlofsky et al. (see fig. 3 ref. [19]). Unfortunately we cannot compare our results in further detail because they have not presented tabulated results. We present some results for nearly touching spheres in table V. In the case of touching spheres, x=0.5, we have calculated a limiting value, λ=0.556. The maximum value of the upper limit is L=15. Durlofsky et al. discussed the existence of a minimum of λ near x≈0.495. This minimum of λ means that the sedimentation velocity of the cluster is maximal. One of their arguments is the existence of such a minimum in the two particle analogue, as shown by Batchelor [21]. Up to this order we were not able to pass around this minimum, although we too believe that this minimum of λ exists. Using the method presented in chapter 3, we can round this minimum in the two particle case, but for values L>20 only. For the maximum value of L used in our calculations, L=150, we have obtained correct results up to x=0.4995. The result for x=0.4995 is 0.713(6) with uncertainty in the decimal between brackets. Jeffrey and Onishi have presented expressions derived from lubrication theory [22]. For the two particle case, as described above, lubrication theory gives: 0.713(1). We expect that also in the three particle problem it must be possible to round the minimum, but we have to use higher values of the upper limit L then. Concerning the results presented in table V we want to point out that we are able to determine λ in the case of small interparticle spacings in contrast with the results of Kim [20]. He has given two possible arguments to explain the divergence behaviour of his results for λ: in the first place he has pointed out that it might be inherently impossible to obtain results for λ in terms of a single expansion in a/R and secondly he has not ruled out an error in his analysis. Our expression for λ can be expressed as a fraction of expansions in a/R so we cannot decide if one of the reasons of Kim is correct to explain the divergence behaviour.

Furthermore it is noteworthy that the pure three particle contribution to the

TABLE V

a/R_{12}	L	λ
0.48	10	0.5607
	12	0.5608
	15	0.5609
0.49	10	0.5572
	12	0.5575
	15	0.5578
0.495	10	0.5558
	12	0.5563
	15	0.5567
0.4975	10	0.5551
	12	0.5557
	15	0.5564
0.5	10	0.5546
	12	0.5553
	15	0.5562

components of the grand mobility matrix, although relatively small for large interparticle distances, become very important in calculating three particle configuration averages. This has consequences when we study the virial expansions of e.g. the translational and rotational short time self–diffusion coefficients D_s^t and D_s^r. In section 4 we present the results of the virial expansions of the self–diffusion coefficients; in section 5 the virial expansions of the sedimentation velocity, U_s/U_o, and its rotational counterpart, Ω_s/Ω_o.

5.4 Translational and rotational self–diffusion, three particle effects

The study of the transport coefficients of suspensions is often aimed at the determination of the virial expansions of these coefficients. In chapter 3 we have explained how virial expansions can be derived, by using pair hydrodynamic interactions between the spherical particles. We have used the pair distribution function up to order φ, the volume

fraction of dispersed particles in the suspension. Some of the results are new and other results had already been obtained by others. We can think e.g. of the first order virial coefficients of the short time translational self–diffusion tensor and of the sedimentation velocity, obtained by Batchelor [21], and of the first order virial coefficient of the short time rotational self–diffusion tensor, obtained by Cichocki and Felderhof [23]. The results for the translational and rotational self–diffusion tensors are

$$\mathbf{D}_s^t = D_o^t \mathbf{I}(1-1.83\varphi-1.13\varphi^2)\,, \tag{5.23}$$

$$\mathbf{D}_s^r = D_o^r \mathbf{I}(1-0.63\varphi-1.02\varphi^2)\,, \tag{5.24}$$

where $D_o^t=k_BT/(6\pi\eta_o a)$, $D_o^r=k_BT/(8\pi\eta_o a^3)$, k_B the Boltzmann constant and T the absolute temperature. The virial expansions of the translational and rotational sedimentation velocities are

$$U_s/U_o = (1-6.55\varphi+12.51\varphi^2)\,, \tag{5.25}$$

$$\Omega_s/\Omega_o = (1-1.52\varphi-0.79\varphi^2)\,, \tag{5.26}$$

with U_o and Ω_o the translational and rotational sedimentation velocity of one particle in an unbounded fluid respectively. Our aim in this section is to correct the second order virial coefficients by including three particle hydrodynamic interactions.

The short time self–diffusion tensors $\mathbf{D}_s^t$ and $\mathbf{D}_s^r$ can be defined by means of the grand mobility matrix. These diffusion tensors can be used to describe the translational and rotational diffusion of a single test particle on a time scale in which the particle configuration remains nearly constant and are defined in the following way:

$$\mathbf{D}_s^t = \frac{k_BT}{N} < \sum_{i=1}^{N} \boldsymbol{\mu}_{ii}^{tt} >_c = k_BT < \boldsymbol{\mu}_{11}^{tt} >_c\,, \tag{5.27}$$

$$(5.28)\qquad D_s^r = \frac{k_B T}{N} < \sum_{i=1}^{N} \mu_{ii}^{rr} >_c = k_B T < \mu_{11}^{rr} >_c ,$$

with N the number of particles in the suspension and $<\cdots>_c$ denotes an average over all configurations of the N particles inside a volume V. The configuration average of the mobility tensors can be rewritten in the following form, where we restrict ourselves for the moment to the translational case,

$$(5.29)\qquad <\mu_{11}^{tt}>_c = \mu_o^t \mathbf{I} + \sum_{n=2}^{N} <[\mu_{11}^{tt}]_n>_c ,$$

where $\mu_o^t = 1/(6\pi\eta_o a)$ and $<[\mu_{11}^{tt}]_n>_c$ denotes a configuration average of the n particle cluster. The average $<[\mu_{11}^{tt}]_2>_c$ is, up to order φ^2, already known (see eq. (5.23)) and if we restrict ourselves to three particle hydrodynamic interactions only, we have to calculate $<[\mu_{11}^{tt}]_3>_c$. The configuration average of the three particle cluster can be evaluated with the help of the following simple three particle distribution function:

$$(5.30)\quad g(\underline{R}_{12},\underline{R}_{13},\underline{R}_{23}) \equiv g(R_{12},R_{13},R_{23}) = \begin{cases} 0 , & R_{12}<2a \text{ or } R_{13}<2a \text{ or } R_{23}<2a \\ 1 , & \text{elsewise} \end{cases} ,$$

with $R_{ij}=|\underline{R}_{ij}|$. It should be noted that $\underline{R}_{23}$ is a function of the interparticle distances $\underline{R}_{12}$ and $\underline{R}_{13}$. Despite the simplicity of the three particle distribution function the configuration integral itself is an integral over a very complicated domain. The configuration average of the three particle cluster is now

$$(5.31)\quad <[\mu_{11}^{tt}]_3>_c = \tfrac{1}{2}\frac{(N-1)(N-2)}{V^2}\int d\underline{R}_{12}\int d\underline{R}_{13} g(R_{12},R_{13},R_{23})[\mu_{11}^{tt}(\underline{R}_{12},\underline{R}_{13})]_3$$

$$= n_o^2 \frac{4\pi^2}{3}\int R_{12}^2 dR_{12}\int R_{13}^2 dR_{13}\int \sin\xi_{13} d\xi_{13}\left[g(R_{12},R_{13},R_{23})\mathrm{Tr}[\mu_{11}^{tt}(\underline{R}_{12},\underline{R}_{13})]_3\right] ,$$

where we have assumed that N>>1. Furthermore we have used rotational symmetries to determine the integrations over the azimuthal angles φ_{12} and φ_{13}, and over the angle ξ_{12}.

Beenakker has calculated the configuration average of the first term of the power expansion in inverse interparticle distances, eq. (5.18a). This integral was evaluated numerically where he used Monte Carlo techniques [7]. The average leads finally to the following three particle contribution of the self–diffusion tensor:

$$[D_s^t]_3 = 1.80\varphi^2 D_o^t \mathbf{I} \,. \tag{5.32}$$

This is slightly lower than the result of an analytical determination of the configuration average,

$$[D_s^t]_3 = 1.81\varphi^2 D_o^t \mathbf{I} \,. \tag{5.33}$$

In this special case there is no essential difference between eq. (5.32) and eq. (5.33) in contrast with the sedimentation problem where it is difficult to evaluate some kind of integrals because of numerical problems. The remaining part of the configuration average of $[\mu_{11}^{tt}]_3$ will be calculated numerically which should be done very carefully, because the three particle contribution of the components of the mobility matrix of particle 1 is strongly influenced by two nearly touching spheres at a great distance from the first particle. In that situation there is also the problem that the components of the mobility matrix of particle 1 have a poor convergence behaviour with increasing L, the upper limit of our set of linear equations. Consequently we have to take into account this area in the numerical integration with great care. This can be done by considering symmetry arguments, viz.

$$\mu_{11}^{tt}(\underline{R}_{12},\underline{R}_{13}) = \mu_{22}^{tt}(\underline{R}_{12},\underline{R}_{23}) \,. \tag{5.34}$$

With this relation we can rewrite the configuration integral and the result is

$$(5.35)\quad <[\mu_{11}^{tt}]_3>_c = \tfrac{1}{2}n_o^2\int d\underline{R}_{12}\int d\underline{R}_{13}H(R_{23}-R_{13})g(R_{12},R_{13},R_{23})\left[[\mu_{11}^{tt}]_3+[\mu_{22}^{tt}]_3\right]$$

$$= \mu_o^t I\varphi^2(\epsilon_1^t+\epsilon_2^t)\,.$$

The function H(x) is the Heaviside function with H(x)=1 if x>0 and H(x)=0 if x<0. The coefficients ϵ_1^t and ϵ_2^t are the virial coefficients obtained from both configuration integrals.

TABLE VI $\quad (ID_o^t\varphi^2[\tilde{D}_s^t]_3=[D_s^t]_3;\ ID_o^r\varphi^2[\tilde{D}_s^r]_3=[D_s^r]_3)$

L	ϵ_1^t	ϵ_2^t	$[\tilde{D}_s^t]_3$	ϵ_1^r	ϵ_2^r	$[\tilde{D}_s^r]_3$
2	0.044	−0.604	1.25	0.218	−0.046	0.17
3	0.235	−0.880	1.17	0.320	−0.075	0.25
4	0.271	−1.015	1.07	0.353	−0.086	0.27
5	0.285	−1.085	1.01	0.366	−0.092	0.27
6	0.293	−1.124	0.98	0.373	−0.097	0.28
7	0.297	−1.147	0.96	0.378	−0.100	0.28
8	0.300	−1.162	0.95	0.381	−0.102	0.28
9	0.301	−1.171	0.94	0.384	−0.104	0.28
10	0.302	−1.178	0.93	0.386	−0.105	0.28

The results of these coefficients are presented in table VI where we see that ϵ_2^t is relatively large and shows slow convergence behaviour. Despite these numerical problems we can make an estimate of the pure three particle contribution of the virial expansion of D_s^t,

$$(5.36)\qquad [D_s^t]_3 = 0.93\varphi^2 D_o^t I\,,$$

which is approximately 50% lower than the value obtained by Beenakker (see in this context his remarks concerning the higher order corrections [6]). The final expression of the virial expansion of D_s^t is now

$$(5.37)\qquad D_s^t = D_o^t I(1-1.83\varphi-0.20\varphi^2)\,,$$

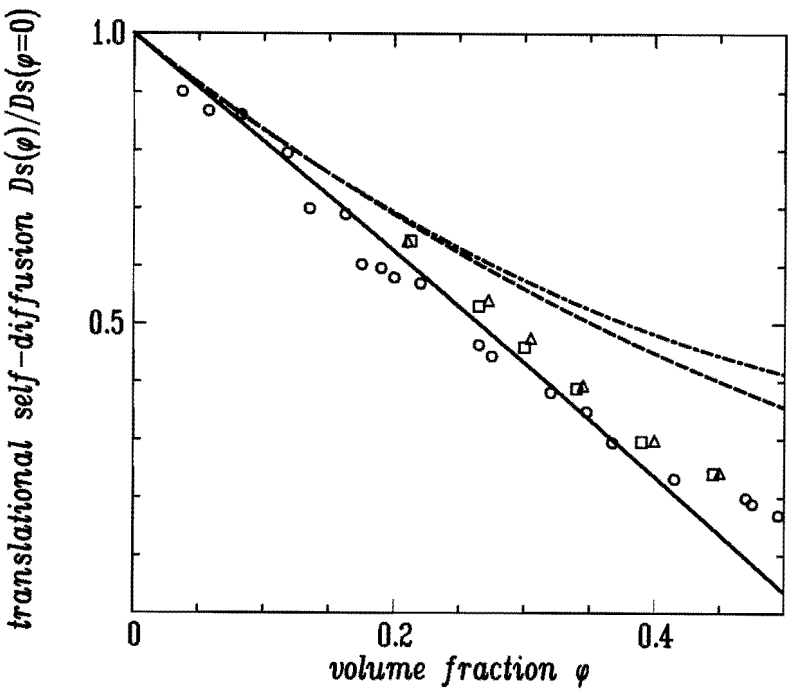

Fig.1. *The short time self–diffusion coefficient, normalized with D_o^t, is plotted versus φ, the volume fraction. The solid curve represents our result, eq. (5.37), the dashed curve represents the virial expansion obtained by Beenakker and Mazur and the dashed–dotted curve represents the virial expansion obtained by Jones et al. The symbols represent experimental results of van Megen and Underwood (circles), Ottewill and Williams (triangles) and Pusey and van Megen (squares).*

where we should take into account that the value of the second order virial coefficient might be some few hundredth parts lower. It is obvious that our value of the second order virial coefficient is much lower than Beenakker's value, 0.88. The difference can partially be explained by the fact that Beenakker has used a value –0.92 instead of –1.13 for the two particle contribution to the second order virial coefficient. Recently Jones, Muthukumar and Cohen have obtained a value of the second order virial coefficient which is even higher

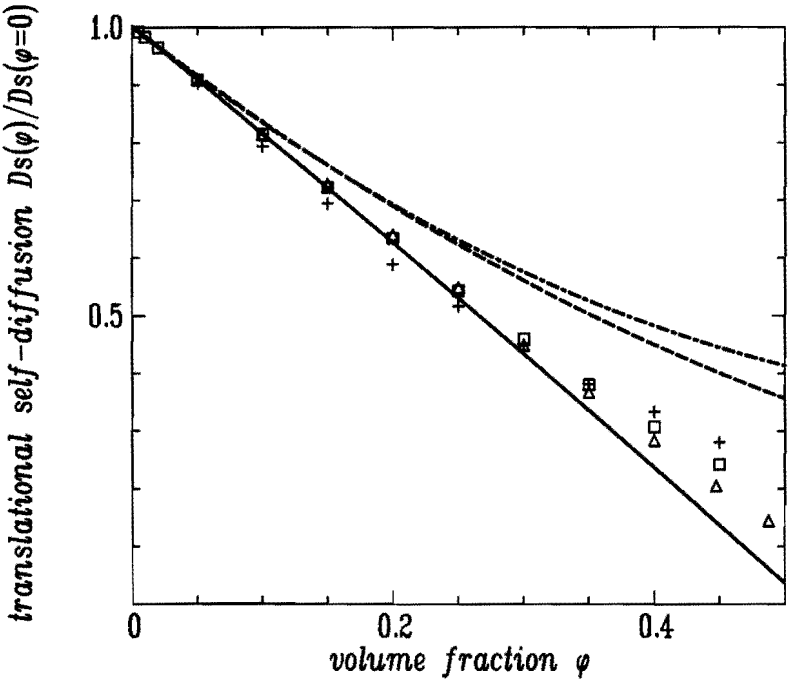

Fig.2. *The short time self–diffusion coefficient, normalized with D_o^t, is plotted versus φ, the volume fraction. The solid curve represents our result, eq. (5.37), the dashed curve represents the virial expansion obtained by Beenakker and Mazur and the dashed–dotted curve represents the virial expansion obtained by Jones et al. The open symbols represent numerical results from Ladd (squares) and simulation data from Phillips et al. (triangles). The plusses represent the results obtained by Beenakker and Mazur, which includes many particle hydrodynamic interactions.*

than Beenakker's value, 1.21 [16]. We cannot explain this difference. In fig. 1 we have plotted our result, Beenakker's result, the result of Jones et al. and some experimental results of Pusey and van Megen [24], Ottewill and Williams [25] and van Megen and Underwood [26]. In fig. 2 we have plotted our result, the numerical results of Ladd [3], the simulation data of Phillips et al. [2] and the result of D_s^t obtained by Beenakker and Mazur,

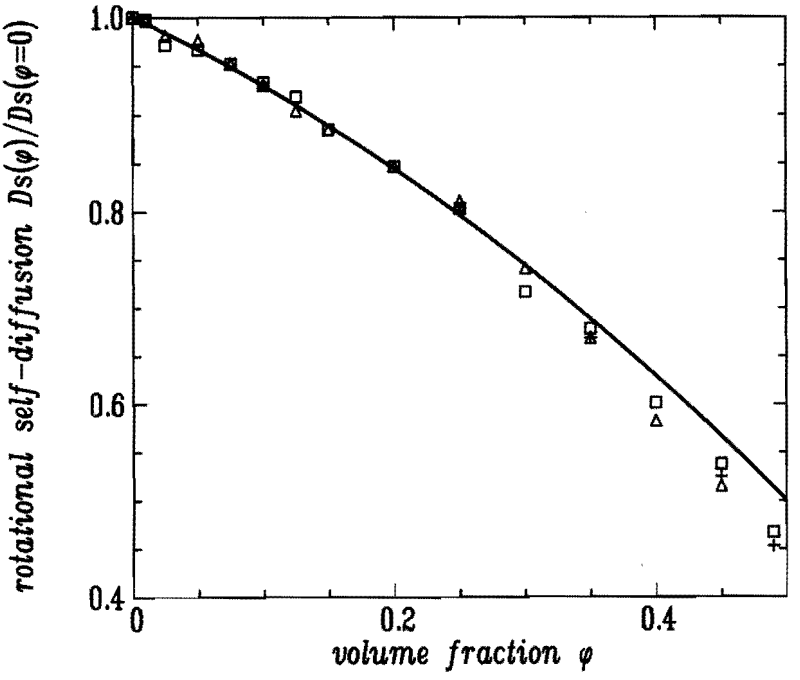

Fig.3. *The short time rotational self–diffusion coefficient, normalized with D_o^r, is plotted versus φ, the volume fraction. The solid curve represents our result, eq. (5.38), and the squares, triangles and plusses represent simulation results of Phillips et al.*

where they used an expansion in powers of the fluctuation in the concentration of the suspended particles [6]. We may conclude that our expression is reasonable up to $\varphi \approx 0.4$, especially if we compare our result with the most recent experiments of van Megen and Underwood, and we may hope that the contribution of four and more particle hydrodynamic interactions to the virial expansion will be an improvement if $\varphi \gtrsim 0.4$. The result of Jones et al. [16] seems too high as well as the virial expansion of Beenakker [6]. Beenakker has already made this conclusion concerning his virial expansion and developed a new method to include many particle hydrodynamic interactions (fig. 2). The numerical data of Ladd and the simulation results of Phillips et al. confirm our remarks above.

In the same way we can determine the virial expansion of D_s^r. This can completely be achieved by numerical means. The results of the numerical integrations are, for different values of L, presented in table VI. The virial expansion, including three particle hydrodynamic interactions, is

$$D_s^r = D_o^r I(1-0.63\varphi-0.74\varphi^2)\,. \tag{5.38}$$

In chapter 3 we pointed out that the three particle contribution to the rotational self–diffusion coefficient would be less important than in the translational case. This is confirmed by considering the two contributions, $0.28\varphi^2$ for $[D_s^r]_3$ and $0.93\varphi^2$ for $[D_s^t]_3$. In fig. 3 we have plotted our expression for the virial expansion of D_s^r and compare this with computer simulation results of Phillips et al. We can conclude that eq. (5.38) corresponds reasonably well with the computer simulation data. Unfortunately there are no experimental results available.

5.5 Translational and rotational sedimentation, three particle effects

The derivation of an expression of the sedimentation velocity is more complicated. In chapter 3 we have used an expression of Pusey and Tough [27] of the short time effective diffusion coefficient to determine the virial expression of the sedimentation velocity. This expression has the following form:

$$D_{eff}(k) = \frac{k_B T}{NS(k)} \sum_{\substack{i=1 \\ j=1}}^{N} \langle \hat{k}\cdot\mu_{ij}^{tt}\cdot\hat{k} \exp(i\underline{k}\cdot\underline{R}_{ij})\rangle_c\,, \tag{5.39}$$

with $\underline{k}$ a wave vector with direction $\hat{k}$ and S(k) the static structure factor. Using eq. (5.31)

and taking $\hat{k}=\hat{e}_z$ we write the three particle contribution as

$$(5.40)\qquad [D_{eff}(k)]_3 = \frac{[D_s^t]_3}{S(k)} + 2\pi^2 n_o^2 \frac{k_B T}{S(k)} \int R_{12}^2 dR_{12} \int R_{13}^2 dR_{13} \int \sin(\xi_{13}) d\xi_{13}$$

$$\times\, g(R_{12},R_{13},R_{23}) \Big[(f(kR_{12})-h(kR_{12})) \Big[[\mu_{12,xx}^{tt}]_3 + [\mu_{12,yy}^{tt}]_3 \Big] + 2h(kR_{12}) [\mu_{12,zz}^{tt}]_3 \Big] ,$$

$$\equiv \frac{[D_s^t]_3}{S(k)} + \frac{k_B T}{S(k)} <\mu_{12}^{tt}, \underline{k}>_c$$

with

$$f(kR) = \frac{2\sin(kR)}{kR}, \quad h(kR) = \frac{2\sin(kR)}{kR} + \frac{4\cos(kR)}{k^2R^2} - \frac{4\sin(kR)}{k^3R^3} .$$

The shorthand notation $<\mu_{12}^{tt}, \underline{k}>_c$ is introduced for later use. The sedimentation velocity is now defined as:

$$(5.41)\qquad U_s/U_o = \lim_{k\to 0} \frac{D_{eff}^t(k)S(k)}{D_o^t} .$$

The calculation of the three particle contribution to U_s/U_o will be achieved in two steps, an analytical and a numerical step. First we write the mobility tensor $[\mu_{12}^{tt}]_3$ in the following way:

$$(5.42)\qquad [\mu_{12}^{tt}]_3 = ([\mu_{12}^{tt}]_3 - \nu_{12}^t) + \nu_{12}^t .$$

The configuration average of ν_{12}^t, defined as in eq. (5.40), will be determined analytically and the same kind of configuration average of the tensor $([\mu_{12}^{tt}]_3 - \nu_{12}^t)$ will be calculated numerically. The tensor ν_{12}^t consists of four terms, which have the following form according to Mazur and van Saarloos [5],

(5.43a) $$(\nu_{12}^t)_1 = \tfrac{15}{8}\mu_o^t\, x_{13}^2 x_{23}^2 (1-3\zeta_3^2)\hat{R}_{13}\hat{R}_{23} ,$$

(5.43b) $$(\nu_{12}^t)_2 = -3\mu_o^t\Big[x_{13}^2 x_{23}^4\Big[2\zeta_3\hat{R}_{13}\hat{R}_{13} + (1-5\zeta_3^2)\hat{R}_{13}\hat{R}_{23}\Big] + x_{13}^4 x_{23}^2\Big[2\zeta_3\hat{R}_{23}\hat{R}_{23} + (1-5\zeta_3^2)\hat{R}_{13}\hat{R}_{23}\Big]\Big] ,$$

(5.43c) $$(\nu_{12}^t)_3 = \tfrac{1}{64}\mu_o^t\, x_{13}^3 x_{23}^3\Big[(49-117\zeta_3^2)I - (93-315\zeta_3^2)(\hat{R}_{13}\hat{R}_{13}+\hat{R}_{23}\hat{R}_{23}) + (783-1575\zeta_3^2)\zeta_3\hat{R}_{13}\hat{R}_{23}\Big] ,$$

(5.43d) $$(\nu_{12}^t)_4 = \tfrac{75}{8}\mu_o^t\Big[x_{12}^2 x_{23}^5 (1-3\zeta_2^2)\hat{R}_{12}\hat{R}_{23} - x_{12}^2 x_{13}^5 (1-3\zeta_1^2)\hat{R}_{12}\hat{R}_{13}\Big] ,$$

with ζ_1, ζ_2 and ζ_3 defined as below eq. (5.18). We shall furthermore use the special coordinate system introduced in section 3. The configuration average of the sum of $(\nu_{12})_i$ is, in the limit k→0,

(5.44) $$\lim_{k\to 0}\ \sum_{i=1}^{4} <(\nu_{12}^t)_i,\underline{k}>_c = 8.0\mu_o^t\varphi^2 .$$

The numerical calculation of the remaining term in eq. (5.42) gives the following contribution:

(5.45) $$<([\mu_{12}^{tt}]_3-\nu_{12}^t),\underline{k}>_c = -0.6\mu_o^t\varphi^2 .$$

In table VII we present the numerical results of the virial coefficients, denoted by ϵ^t, for different values of the upper limit L. This gives us some understanding of the convergence behaviour of the numerical coefficient in eq. (5.45). The total three particle contribution of the virial expansion of the sedimentation velocity is now $<[\mu_{12}^{tt}]_3,\underline{k}>_c = 7.4\mu_o^t\varphi^2$, and the virial expansion, including the three particle contribution to the self–diffusion coefficient, is

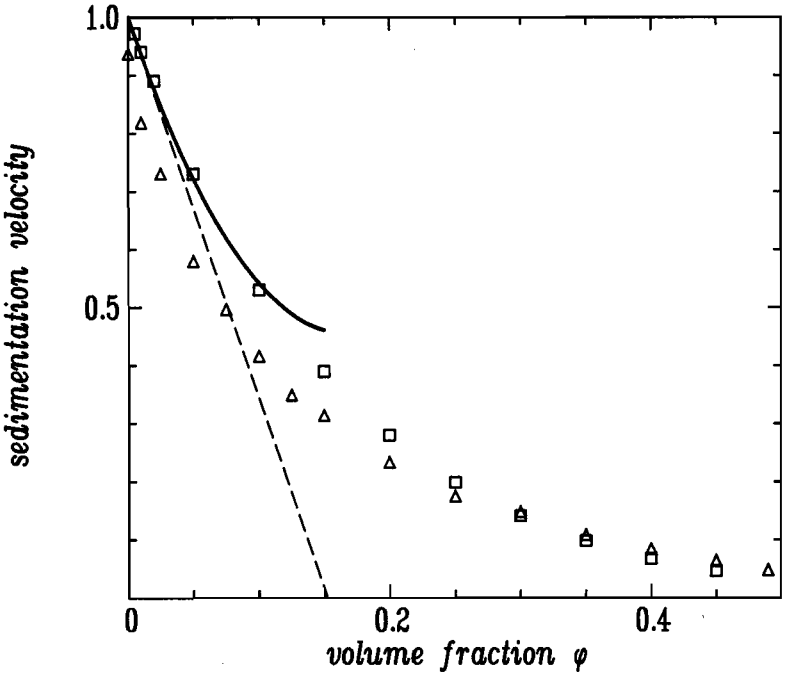

Fig.4. *The sedimentation velocity, normalized by its infinite dilution value U_o, is plotted versus φ. The bold solid curve represents our result (up to φ=0.15) and the thin dashed line represents the Batchelor expression. The squares represent numerical data of Ladd and the triangles represent the results of Phillips et al.*

(5.46) $$U_s/U_o = 1-6.55\varphi+19.7\varphi^2 .$$

We have compared this result with numerical results obtained by Ladd [3] and computer simulation results of Phillips, Brady and Bossis [2]. We have plotted these results in fig. 4. The data of Phillips et al. differ, for small φ, with our result and the results obtained by Ladd. This difference is caused by the insertion of a degree of periodicity into the model of Phillips et al. (see also ref. [2]). In fig. 4 we have plotted also the linear virial expansion (the Batchelor expression) and we can conclude that this expression describes

TABLE VII

L	ϵ^t	ϵ^r
2	+0.80	−0.042
3	−0.20	+0.040
4	−0.40	+0.009
5	−0.50	−0.005
6	−0.55	−0.012
7	−0.57	−0.015
8	−0.59	−0.016
9	−0.60	−0.017
10	−0.61	−0.017

sedimentation reasonably well up to $\varphi \approx 0.05$. Our expression (eq. (5.46)) is reasonable up to $\varphi \approx 0.12$–0.13. Beyond this value of φ the virial expansion describes sedimentation very badly and it can be expected that the third order virial coefficient should be large (comparable with the second virial coefficient) and negative to compensate the quadratic term. We have not plotted experimental results in fig. 4. These results are of course available, but some recent experimental results from Buscall et al. [28] and Bacri et al. [29] resemble the numerical data of Ladd very well up to $\varphi \approx 0.5$. Recently Jones et al. [16] have presented results of the second order virial coefficient and their virial expansion has the following form:

$$U_s/U_o = 1-6.57\varphi+18.27\varphi^2 . \tag{5.47}$$

Their virial expansion resembles ours, although the three particle contribution of this expression is nearly 20% lower than in our result. The difference becomes larger if we split off in both results the three particle contribution belonging to the self–diffusion coefficient. The result of Jones et al. [16] is then 4.6, which is nearly 40% lower than our result, viz. 7.4. As is the case with the three particle contribution to the self–diffusion coefficient we cannot explain this difference.

In an analogous way we have studied the virial expansion of the rotational

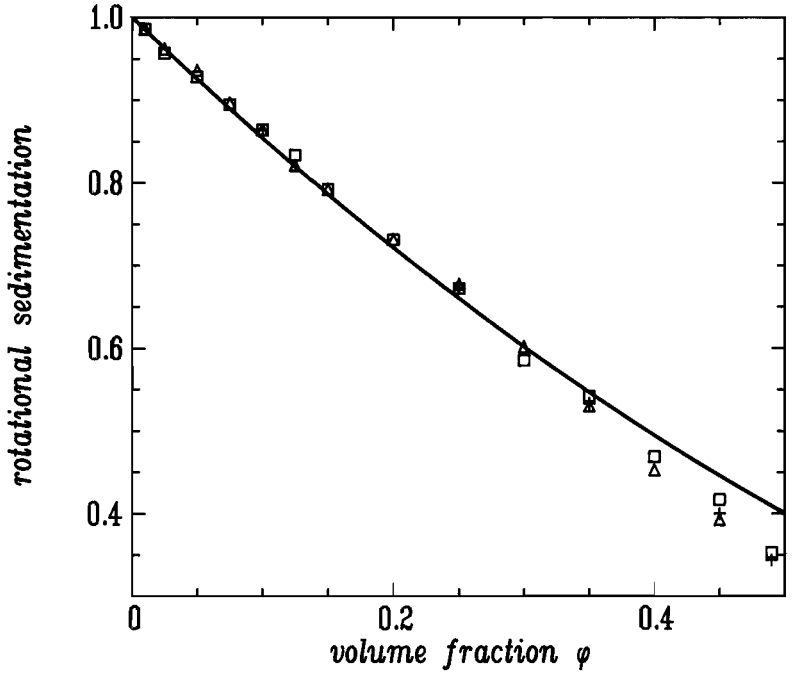

Fig.5. *The rotational velocity, normalized by its infinite dilution value Ω_o, is plotted versus φ. The bold solid curve represents our result, eq. (5.51), and the squares, triangles and plusses represent simulation results of Phillips et al.*

counterpart of sedimentation. The only difference is that μ^{tt} should be replaced by μ^{rr} in the equations above. Here we have to calculate one term analytically, viz. [5]

$$[\mu_{12}^{rr}]_3 = ([\mu_{12}^{rr}]_3 - \nu_{12}^{r}) + \nu_{12}^{r}\,, \tag{5.48}$$

with

$$\nu_{12}^{r} = \tfrac{15}{4}\mu_o^{r}\, x_{13}^3 x_{23}^3 \left[(\hat{R}_{13}\times\hat{R}_{23})(\hat{R}_{13}\times\hat{R}_{23}) + \zeta_3 \hat{R}_{23}\hat{R}_{13} - \zeta_3^2 \mathbf{I}\right] \tag{5.49}$$

and $\mu_o^{r}=1/(8\pi\eta_o a^3)$. The configuration average of ν_{12}^{r} is

$$(5.50) \qquad <\nu^{r}_{12},\underline{k}>_{c} = 1.17\mu^{r}_{o}\varphi^{2} .$$

The numerical calculation of the remaining part yields the contribution $-0.02\mu^{r}_{o}\varphi^{2}$. In table VII the numerical result is tabulated as a function of the upper limit L. The virial expansion of Ω_s/Ω_o is

$$(5.51) \qquad \Omega_s/\Omega_o = 1-1.52\varphi+0.64\varphi^{2} .$$

In fig. 5 we have plotted this result as a function of volume fraction φ and compared the result with computer simulation results of Phillips et al. [2]. This virial expansion and the simulation results agree very well up to $\varphi\approx 0.4$, which leads to the conclusion that rotational sedimentation can be described reasonably well by using two and three particle hydrodynamic interactions between the hard spheres in a suspension.

5.6 Conclusion

The set of linear equations derived in chapter 2 has been used to study three particle hydrodynamic interactions. After studying some components of the grand mobility matrix one important conclusion can be drawn, namely that it is necessary to include many terms of the power expansion in typical inverse interparticle distances to describe three particle hydrodynamic interactions sufficiently, even at intermediate interparticle distances. This is a tedious task and as far as we know there are no results available of arbitrary configurations of the three particle cluster. The method presented in this chapter seems more attractive to perform these calculations, although the final result is not in the form of a single power expansion. Analytical expressions can be obtained by using algebraic computer programmes. We have restricted ourselves to calculating these components

numerically.

The study of the three particle contribution to the translational self–diffusion coefficient leads to the conclusion that the contribution calculated in section 4 (eq. (5.36)) is much smaller than predicted by several other authors, but the derived expression of $\mathbf{D}_s^t$ (eq. (5.37)) is reasonable, if compared with experimental data and simulation results, up to $\varphi \approx 0.4$ in contrast with expressions derived by Beenakker [7] and Jones et al. [17]. The rotational counterpart is described reasonably well using two and three particle hydrodynamic interactions only. This is also the case for the rotational sedimentation. At this moment we can compare these theoretical results with simulation data only because, to our knowledge, there are no experimental results available. Translational sedimentation cannot be described very easily in terms of a virial expansion. With the expression derived in this chapter (eq. (5.46)) we can extend the range where that expression is reasonable to higher volume fractions, up to $\varphi \approx 0.13$. For higher volume fractions we cannot use this virial expansion. Despite this disappointing result, which was expected, we can learn something different from it and also from the result of Jones et al. [17]. Both results show that it is dangerous to derive virial coefficients from experimental results with fitting procedures. There are several results of the second order virial coefficient of sedimentation available, obtained from experiment. Kops–Werkhoven and Fijnaut obtained the value 10 ± 4 [30], which is too small, and Cheng and Schachman obtained a value of roughly 20 [31], which is reasonable. The same remark is also valid for other virial expansions, like the virial expansion of the translational self–diffusion coefficient.

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Chapter 6 BROWNIAN MOTION AND LONG TIME TAILS

6.1 Introduction

The theory of Brownian motion has been and still is a field of intensive research. Some aspects of present day research have already been mentioned in the preceding chapters like the study of the self–diffusion coefficient in the chapters 3 and 5. We have also mentioned the effect of Brownian motion on the behaviour of the low shear rate effective viscosity of suspensions. In the area of computational physics a new sub–discipline has been developed called Brownian dynamics. In this chapter we present some results of a study of the correlation functions of Brownian particles in an unbounded fluid with or without an externally imposed shear flow and some results of a study of such particles in a harmonic potential. The mean square displacement of these particles can be studied, and in connection with it the diffusion of the Brownian particles if a diffusional regime exists. For the moment we assume that hydrodynamic interactions are absent. Before we come to these points we give a short historical review.

In 1827 Robert Brown, a Scottish botanist, observed under the microscope the random motion of pollen grains. This was the starting point of the study of Brownian motion. In the beginning of this century some important steps in the development of the theory of Brownian motion were set by Einstein [1] and Langevin [2]. Einstein presented a relation between the diffusion coefficient D_o of a spherical Brownian particle and the Stokes friction coefficient ζ, nowadays known as the Stokes–Einstein relation,

$$D_o = \frac{k_B T}{\zeta}, \tag{6.1}$$

where $\zeta=6\pi\eta_o a$ with η_o the shear viscosity of the fluid and a the radius of the spherical Brownian particle. Moreover, k_B is the Boltzmann constant and T is the absolute temperature. This relation has been derived by using thermodynamical arguments. Besides the above mentioned result, Einstein defined the following relation between the diffusion coefficient D_o and the velocity autocorrelation function $\phi(t)$, although he did not use this relation to obtain eq. (6.1),

$$D_o = \lim_{t\to\infty} \frac{<x^2(t)>}{2t} = \int_0^\infty \phi(t)dt \,, \tag{6.2}$$

where $<x^2(t)>$ is the mean square displacement. It is obvious that the long time behaviour should be such that $t\phi(t)\to 0$ if $t\to\infty$. In the same period Langevin used another method to study diffusion of Brownian particles. He introduced an equation of motion for free Brownian particles:

$$m\dot{\underline{U}}(t) = -\zeta\underline{U}(t) + \underline{R}(t) \tag{6.3}$$

with m the mass of the particle, $\underline{U}(t)$ its velocity and $\underline{R}(t)$ is a random force exerted by the fluid molecules in collisions with the Brownian particle. The random force is assumed to be Gaussian, $<\underline{R}(t)>=\underline{0}$, where $<\cdot\cdot>$ denotes an ensemble average. Furthermore,

$$<R_i(t)R_j(t')> = 2\zeta k_B T\delta_{ij}\delta(t-t') \,, \tag{6.4}$$

which means that successive collisions of fluid molecules are uncorrelated. With the Langevin equation an explicit expression for the velocity autocorrelation function can be derived, which, in this case, is an exponentially decaying function of time [3],

$$\phi(t) = \frac{k_B T}{m} \exp(-\frac{\zeta}{m}t) \,. \tag{6.5}$$

In the years following these important developments several other authors have presented results of studies of the behaviour of Brownian particles. We think of the work of Uhlenbeck and Ornstein who studied among other things the behaviour of Brownian particles in a harmonic potential [4]. Much work on the general theory of Brownian motion has been reviewed by Chandrasekhar [5] and Wang and Uhlenbeck [6].

In the sixties several publications concerning computer simulations to study the behaviour of fluid molecules were published. Both Rahman [7,8] and Alder and Wainwright [9–11] found in computer experiments, where they simulated the motion of a tagged particle in a hard sphere fluid, that the velocity autocorrelation function of that tagged particle has a long time tail, instead of showing an exponential decay, viz.

$$\phi(t) \approx Ct^{-3/2}, \quad t>>\tau_B, \tag{6.6}$$

with $\tau_B=(6\pi\eta_o a/m)t$ and C a constant. Eq. (6.6) is valid in the case of a three dimensional hard sphere fluid. In general they obtained a long time tail behaviour $t^{-d/2}$, with d the dimensionality of the system. In one and two dimensional systems this long time tail leads to divergencies in Green–Kubo integrals like eq. (6.2). Alder and Wainwright were able to explain the long time tail in eq. (6.6) for three dimensional hard sphere fluids by considering the cooperative effect from the surrounding fluid molecules, which could be described by macroscopic hydrodynamics [10,11]. This explanation was also given by Zwanzig and Bixon [12]. Widom studied the behaviour of a Brownian particle in a viscous fluid by using the generalized Langevin equation, a Langevin equation with a memory kernel, viz.

$$m\dot{\underline{U}}(t) = -\int_{-\infty}^{t} \zeta(t-\tau)\underline{U}(\tau)d\tau + \underline{R}(t) . \tag{6.7}$$

Apart from the different form of the Langevin equation it is important to note that the

collisions of the fluid molecules with the Brownian particle are correlated, and consequently the random force autocorrelation function is not proportional to the Dirac delta function anymore, although the random force remains Gaussian. Widom was able to solve this problem analytically and showed the existence of the long time tail in the velocity autocorrelation function of the Brownian particle [13]. Since that time several other authors have studied this problem [14–18] as well as the rotational counterpart of this function [19–21]. Ailawadi and Berne showed the following long time behaviour of the angular velocity autocorrelation function [19]:

$$\phi_r(t) \approx Ct^{-5/2}, \quad t >> \tau_B^r, \tag{6.8}$$

with, in the case of spherical particles, $\tau_B^r = \frac{10}{3}\tau_B$. Finally we want to remark that these long time tails in correlation functions of microscopic properties have appeared in many theories and are accepted among statistical physicists (see for a review e.g. Pomeau and Résibois [22]).

In the sections 3 and 4 we present the results of a study of the velocity autocorrelation function and the mean square displacement of Brownian particles in a harmonic potential and in an externally imposed shear flow respectively. We shall concentrate on the backflow effects, which appear explicitly in the generalized Langevin equations, necessary to solve the problems mentioned above. In section 2 we shall review the problem of a free Brownian particle in an unbounded fluid, in order to introduce some general concepts. We shall end this chapter with a short conclusion.

6.2 The free Brownian particle

We present the results of a study of a Brownian particle in an unbounded fluid at rest at infinity. The particle is of such a small size that the Reynolds number of the fluid motion induced by the Brownian particle is small. So we can neglect the non–linear term in the Navier–Stokes equations. The fluid motion is then described by the linearized incompressible time dependent Navier–Stokes equations. There are no external forces acting on the particle. We consider a random force $\underline{R}(t)$ only. This problem can be reduced to a one dimensional problem because of isotropy. The Brownian particle has velocity $U(t)$ if $t>0$, and is assumed to be at rest if $t\leq 0$. The velocity of this particle is determined by its velocity at earlier times via backflow effects in the fluid; the equation of motion is described by the following generalized linear Langevin equation, which is called the Stokes–Boussinesq equation, and can be derived by solving the time dependent Navier–Stokes equations describing the system under consideration [23,24]:

$$(6.9) \qquad m\dot{U}(t) = -6\pi\eta_o a U(t) - \tfrac{1}{2}m_0\dot{U}(t) - 6a^2\sqrt{\pi\rho\eta_o}\int_0^t \frac{1}{\sqrt{t-\tau}}\,\dot{U}(\tau)d\tau + R(t)\,,$$

with ρ the density of the fluid and $m_0 = \frac{4}{3}\pi a^3\rho$ the mass of the fluid displaced by the Brownian particle. Furthermore we introduce the effective mass $M=m+\frac{1}{2}m_0$. The first term of eq. (6.9) is the ordinary Stokes' friction, the second is connected with the virtual mass of a sphere in an incompressible fluid, and the third is a memory term associated with the hydrodynamic retardation effects and related to the penetration depth of viscous unsteady flow around a sphere. This equation can be solved by using the theory of Laplace transforms. The Laplace transform of a function $f(t)$ has the following form [25]:

$$(6.10) \qquad \tilde{f}(s) = \int_0^\infty e^{-st}f(t)dt\,, \quad Re(s)>0\,.$$

Via the Laplace transform of eq. (6.9) we obtain,

$$(6.11) \qquad \tilde{U}(s) = \tilde{A}(s)\tilde{R}(s) , \qquad \tilde{A}(s) = \frac{1}{(Ms+z\sqrt{s}+\zeta)} ,$$

with $z=6\pi a^2\sqrt{\rho\eta_o}$. The Laplace transform of the velocity autocorrelation function is now

$$(6.12) \qquad <\tilde{U}(s)\tilde{U}(s')> = \tilde{A}(s)\tilde{A}(s')<\tilde{R}(s)\tilde{R}(s')> .$$

Taking x(0)=0 and using the fact that the position x(t) is the time integral of the velocity of the Brownian particle we find the position autocorrelation function:

$$(6.13) \qquad <\tilde{x}(s)\tilde{x}(s')> = \tilde{B}(s)\tilde{B}(s')<\tilde{R}(s)\tilde{R}(s')> , \quad \tilde{B}(s) = \tilde{A}(s)/s .$$

This function is used to determine the mean square displacement of the Brownian particle. It is obvious that it is necessary to know a relation between the Laplace transform of the random force autocorrelation function and the function $\tilde{A}(s)$ or $\tilde{B}(s)$ to evaluate the Laplace inverse of both expressions above (eqs. (6.12) and (6.13)). We start with the Fourier transform of the random force autocorrelation function derived by Bedeaux and Mazur. They used a generalized Faxén theorem and obtained [26],

$$(6.14) \qquad <R(\omega)R^*(\omega')> = 4\pi k_B T\delta(\omega-\omega')\left[\zeta + \tfrac{1}{2}z\sqrt{2|\omega|}\right] \equiv 2\pi\theta(|\omega|)\delta(\omega-\omega').$$

From the properties of the equation above we can conclude that the random force autocorrelation function has the following form:

$$(6.15) \qquad <R(t_1)R(t_2)> = \theta(|t_2-t_1|) .$$

The Laplace transform of equation (6.15) is (see ref. [27] p.195),

$$(6.16) \qquad <\tilde{R}(s)\tilde{R}(s')> = \frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} .$$

A simple relation can be derived between $\tilde{\theta}(s)$ and $\tilde{A}(s)$ (eq. (6.11)) [27],

$$(6.17) \qquad \tilde{A}(s)\tilde{\theta}(s) = k_B T(1 - Ms\tilde{A}(s)) ,$$

and the Laplace transform of the velocity autocorrelation function is now,

$$(6.18) \qquad <\tilde{U}(s)\tilde{U}(s')> = k_B T\left[\frac{\tilde{A}(s)+\tilde{A}(s')}{s+s'} - M\tilde{A}(s)\tilde{A}(s')\right] .$$

Inverse Laplace transformation and the use of tables of Laplace transforms [28] result in the following expression:

$$(6.19) \qquad <U(t_1)U(t_2)> = k_B T\left[A(|t_2-t_1|) - MA(t_1)A(t_2)\right] ,$$

with

$$(6.20) \qquad A(t) = \frac{1}{M(b-a)}\left[b\exp(b^2t)\mathrm{erfc}(b\sqrt{t}) - a\exp(a^2t)\mathrm{erfc}(a\sqrt{t})\right] ,$$

$$a = (z + (z^2-4\zeta M)^{1/2})/2M \; ; \quad b = (z - (z^2-4\zeta M)^{1/2})/2M .$$

The function erfc(z) is the complementary error function as defined in [29]. For the moment we assume that $a \neq b$, which means that one special ratio between the density of the particle and the fluid density will not be considered analytically, viz. $\sigma \equiv \rho_s/\rho \neq \frac{5}{8}$. We can come to an expression for the velocity autocorrelation function in that special case by taking the appropriate limits in eq. (6.20) or by rederiving that equation with the function

$\tilde{A}(s)=M^{-1}(\sqrt{s}+a)^{-2}$. We are interested in the stationary part of equation (6.19), which can be obtained by studying the limit $t_1\to\infty$, $t_2\to\infty$, but $t_2-t_1\equiv\tau\geq 0$ remains finite. We can conclude from eq. (6.20) that $A(t)\to 0$ if $t\to\infty$ by considering its asymptotic expansion via

$$\exp(a^2t)\mathrm{erfc}(a\sqrt{t}) \simeq \frac{1}{a\sqrt{\pi}\sqrt{t}} - \frac{1}{2\sqrt{\pi}a^3t\sqrt{t}} + \frac{3}{4\sqrt{\pi}a^5t^2\sqrt{t}} - \frac{15}{8\sqrt{\pi}a^7t^3\sqrt{t}} + O\left(\frac{1}{t^4\sqrt{t}}\right), \quad |a^2|t>>1 . \tag{6.21}$$

It should be noted that both a and b can be complex. Finally we obtain,

$$\langle U(t_1)U(t_1+\tau)\rangle^{\infty} \equiv \phi(\tau) = k_BTA(\tau) , \tag{6.22}$$

where $\langle\cdots\rangle^{\infty}$ denotes the long time limit described above. This result has been obtained by several authors, e.g. Widom [13] and Chow and Hermans [14]. We emphasize that $A(0)=1/M$ and consequently have

$$\lim_{\tau\to 0}\phi(\tau) = \frac{k_BT}{M} . \tag{6.23}$$

This result is in contradiction with the equipartition theorem because the particle mass m instead of the effective mass M would be expected in eq. (6.23). This paradox has been solved by Zwanzig and Bixon [16] (see in this context also ref. [15]). They have shown a rapid initial decrease from k_BT/m to k_BT/M at very short time scales by including compressibility effects in the study of the velocity autocorrelation function. It is easy to determine the long time behaviour of the velocity autocorrelation function, using the asymptotic expansion of the product of the exponential function and complementary error function, eq. (6.21). We obtain for $\phi(\tau)$,

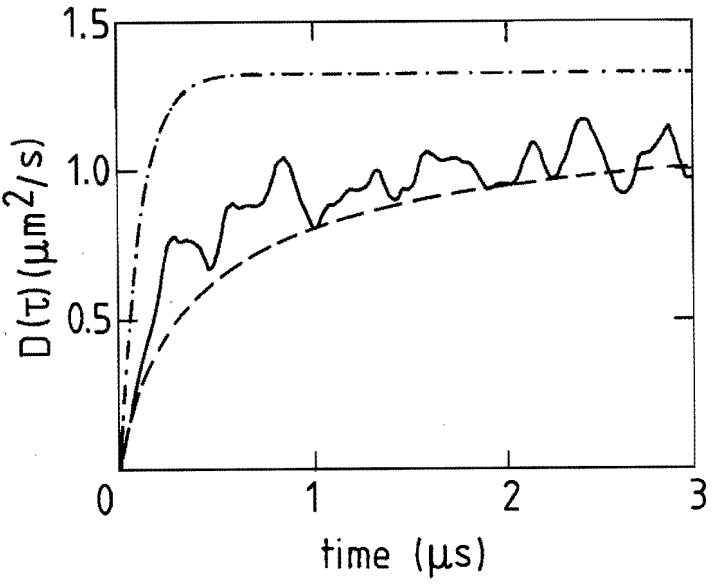

Fig.1. *Time dependent diffusion coefficient as measured by Weitz et al.. Solid line: experiment; dash–dotted line: theory without retardation effects (Stokes limit); dashed line: theory including retardation effects.*

$$(6.24) \qquad \phi(\tau) \simeq k_B T \frac{z}{2\zeta^2\sqrt{\pi}} \frac{1}{\tau\sqrt{\tau}} + O(\frac{1}{\tau^2\sqrt{\tau}}) , \quad |a^2|\tau>>1 \text{ and } |b^2|\tau>>1 ,$$

which shows the famous long time tail.

In an analogous way one can obtain an expression for the position autocorrelation function. Combination of eqs. (6.13) and (6.16) and the use of a relation like eq. (6.17) result in

$$(6.25) \qquad <\tilde{x}(s)\tilde{x}(s')> = k_B T\left[\frac{\tilde{C}(s')}{s} + \frac{\tilde{C}(s)}{s'} - \frac{\tilde{C}(s)+\tilde{C}(s')}{s+s'} - M\tilde{B}(s)\tilde{B}(s')\right] ,$$

where $\tilde{C}(s)=\tilde{B}(s)/s$. The inverse Laplace transform of this relation can be determined with

the tables of Oberhettinger and Badii [28]. We assume that $t_1 \to \infty$, $t_2 \to \infty$, but $t_2 - t_1 \equiv \tau \geq 0$. The mean square displacement is

$$(6.26) \qquad \langle (x(t_1+\tau)-x(t_1))^2 \rangle^{\infty} \equiv \Psi(\tau) = 2k_B T C(\tau) ,$$

$$= 2D_o \left[\tau - \frac{2z}{\zeta\sqrt{\pi}} \sqrt{\tau} + \frac{(z^2-\zeta M)}{\zeta^2} + \frac{\zeta}{M(b-a)} \left[b^{-3} \exp(b^2\tau) \operatorname{erfc}(b\sqrt{\tau}) \right.\right.$$

$$\left.\left. - a^{-3} \exp(a^2\tau) \operatorname{erfc}(a\sqrt{\tau}) \right] \right] ,$$

where $C(0)=0$. D_o is the Stokes–Einstein diffusion coefficient, $D_o = k_B T/\zeta$. This expression has already been presented by Paul and Pusey [30]. Weitz et al. have presented measurements which support this expression [31] (see fig. 1). In the limit of large τ we obtain the familiar result $\Psi(\tau) = 2D_o\tau$.

In the subsequent sections we use these methods, but give less details.

6.3 A Brownian particle in a harmonic potential

We consider a Brownian particle in a harmonic potential. This model can be used to describe a Brownian particle in the equilibrium position of a potential, where small displacements can be assumed to be harmonic. We can think of small charged colloidal particles in a crystal structure. The problem of a Brownian particle confined to a restricted volume can also roughly be described by using a harmonic potential. The equation of motion of such a Brownian particle resembles the Stokes–Boussinesq equation, but we introduce a force $F(t) = -Kx(t)$. As is the case with the problem of the free Brownian particle we can describe the problem under consideration as a one dimensional problem

because there is no coupling with position and velocities of the y– and z–directions. The equation of motion is now, assuming that the particle is at the equilibrium position $x_o=0$ if $t=0$ and at rest for $t\leq 0$,

$$(6.27) \qquad M\dot{U}(t) = -6\pi\eta_o aU(t) - 6a^2\sqrt{\pi\rho\eta_o}\int_0^t \frac{1}{\sqrt{t-\tau}}\dot{U}(\tau)d\tau - Kx(t) + R(t) .$$

The Laplace transform of this equation of motion gives,

$$(6.28) \qquad \tilde{U}(s) = \tilde{A}(s)\tilde{R}(s) , \quad \tilde{A}(s) = \frac{s}{(Ms^2+z\sqrt{s}+\zeta s+K)} ,$$

where ζ and z are defined in section 2. The Laplace transform of the velocity autocorrelation function is,

$$(6.29) \qquad <\tilde{U}(s)\tilde{U}(s')> = \tilde{A}(s)\tilde{A}(s')<\tilde{R}(s)\tilde{R}(s')> .$$

The analogue of eq. (6.17) for a relation between $\tilde{A}(s)$ and $\tilde{\theta}(s)$ is:

$$(6.30) \qquad \tilde{A}(s)\tilde{\theta}(s) = k_BT\left[1 - Ms\tilde{A}(s) - K\tilde{B}(s)\right] ,$$

with the Laplace transform $\tilde{B}(s)=\tilde{A}(s)/s$. With this relation we can write for the velocity autocorrelation function,

$$(6.31) \qquad <\tilde{U}(s)\tilde{U}(s')> = k_BT\left[\frac{\tilde{A}(s)+\tilde{A}(s')}{s+s'} - M\tilde{A}(s)\tilde{A}(s') - K\tilde{B}(s)\tilde{B}(s')\right] .$$

We consider the Laplace inverse in the situation that $t_1\to\infty$, $t_2\to\infty$ but $t_2-t_1\equiv\tau\geq 0$ is finite. We obtain the following velocity autocorrelation function of a Brownian particle in a harmonic potential,

$$(6.32) \qquad <U(t_1)U(t_1+\tau)>^{m} = \phi(\tau) = k_B T A(\tau) ,$$

where the function $A(\tau)$ can be determined with the help of tables of inverse Laplace transforms [28]. This function is

$$(6.33) \qquad A(\tau) = \frac{1}{M}\left[\frac{a^3\exp(a^2\tau)\mathrm{erfc}(a\sqrt{\tau})}{(a-b)(a-c)(a-d)} + \frac{b^3\exp(b^2\tau)\mathrm{erfc}(b\sqrt{\tau})}{(b-a)(b-c)(b-d)}\right.$$

$$\left. + \frac{c^3\exp(c^2\tau)\mathrm{erfc}(c\sqrt{\tau})}{(c-a)(c-b)(c-d)} + \frac{d^3\exp(d^2\tau)\mathrm{erfc}(d\sqrt{\tau})}{(d-a)(d-b)(d-c)}\right] ,$$

where the (complex) coefficients a, b, c and d can be obtained by writing the denominator in the expression of $\tilde{A}(s)$ in the following form:

$$(6.34) \qquad Ms^2+\varkappa s\sqrt{s}+\zeta s+K = M(\sqrt{s}+a)(\sqrt{s}+b)(\sqrt{s}+c)(\sqrt{s}+d) .$$

We assume for the moment that the coefficients a, b, c and d are all different of each other. If two or more coefficients are equal we can follow the procedure mentioned in section 2 below eq. (6.20). We are now interested in the long time behaviour of this expression. Replacement of the complementary error functions in our expression of $A(\tau)$ by the asymptotic expansion (6.21) gives,

$$(6.35) \qquad \phi(\tau) \simeq k_B T \frac{15\varkappa}{8K^2\sqrt{\pi}}\frac{1}{\tau^3\sqrt{\tau}} + O\left(\frac{1}{\tau^4\sqrt{\tau}}\right) , \quad |a^2|\tau >> 1 \text{ etc.}$$

In the derivation of this asymptotic expansion we have used the following relations between the coefficients a to d, which we shall not demonstrate here,

$$(6.36) \qquad \frac{a^n}{(a-b)(a-c)(a-d)} + \frac{b^n}{(b-a)(b-c)(b-d)} + \frac{c^n}{(c-a)(c-b)(c-d)}$$

$$+\frac{d^n}{(d-a)(d-b)(d-c)} = 0 \quad , \quad n\epsilon\{-2,0,2\} \, ,$$

and

$$\frac{a^{-4}}{(a-b)(a-c)(a-d)} + \frac{b^{-4}}{(b-a)(b-c)(b-d)} + \frac{c^{-4}}{(c-a)(c-b)(c-d)}$$

$$+\frac{d^{-4}}{(d-a)(d-b)(d-c)} = -\frac{zM}{K^2} \, .$$

Instead of an exponentially decaying velocity autocorrelation function we have obtained again a long time tail, although this tail has a lower power in $1/\sqrt{\tau}$ in comparison to the free particle case, viz. $\tau^{-7/2}$ versus $\tau^{-3/2}$ respectively. On top of that this long time tail has a positive sign. In the Stokes limit the velocity autocorrelation function has, in the overdamped case ($\zeta >> \sqrt{Km}$), a negative exponentially decaying tail. In the strongly overdamped case two separate time scales can be distinguished. On the smaller the particle does not feel the harmonic force and the behaviour of the velocity autocorrelation function is comparable to the free particle case, including the existence of the $\tau^{-3/2}$ long time tail. Then, at intermediate times, it can be shown by numerical means that eq. (6.32) also has a negative part before the positive $\tau^{-7/2}$ tail becomes dominant. A Brownian particle in a colloidal crystal can be described by the overdamped case discussed above. We use some data of Derksen (ref. [32] p. 40,44). Consider a colloidal crystal in water built up of polystyrene spheres, with radii $a \approx 5 \times 10^{-8}$m, with charge $Q \approx 10^{-16}$C, with a lattice parameter $R \approx 10^{-6}$m and suppose the particle is displaced by an amount $\Delta << R$, then

$$(6.37) \qquad \frac{Q^2}{4\pi\epsilon}\left[\frac{1}{R+\Delta} + \frac{1}{R-\Delta}\right] - \frac{Q^2}{2\pi\epsilon R} \approx \frac{Q^2}{2\pi\epsilon R^3}\Delta^2 \equiv \tfrac{1}{2}K\Delta^2 \, ,$$

or

$$(6.38) \qquad K = \frac{Q^2}{\pi\epsilon R^3} \, ,$$

with $\epsilon=\epsilon_0\epsilon_r\approx 7\times10^{-10}$ ($\epsilon_r\approx80$) the dielectric constant of water. The shear viscosity of water is $\eta_o\approx10^{-3}$Pa s. In this case: $\zeta\approx10^{-9}$N s m^{-1} and $\sqrt{Km}\approx10^{-12}$N s m^{-1}. Later we shall show that there exists a maximum value for Δ, and with the data presented above $\Delta_{max}<<R$.

The position autocorrelation function can be determined in the same way. The final expression is,

$$(6.39)\quad \langle\tilde{x}(s)\tilde{x}(s')\rangle = k_BT\left[\frac{\tilde{C}(s')}{s}+\frac{\tilde{C}(s)}{s'}-\frac{\tilde{C}(s)+\tilde{C}(s')}{s+s'}-M\tilde{B}(s)\tilde{B}(s')-K\tilde{C}(s)\tilde{C}(s')\right],$$

where $\tilde{C}(s)=\tilde{B}(s)/s$. The asymptotic part of the mean square displacement is

$$(6.40)\qquad \langle(x(t_1+\tau)-x(t_1))^2\rangle^{\infty}\equiv\Psi(\tau)=2k_BTC(\tau),$$

with

$$(6.41)\qquad C(\tau)=\frac{1}{K}+\frac{1}{M}\left[\frac{\exp(a^2\tau)\mathrm{erfc}(a\sqrt{\tau})}{a(a-b)(a-c)(a-d)}+\frac{\exp(b^2\tau)\mathrm{erfc}(b\sqrt{\tau})}{b(b-a)(b-c)(b-d)}\right.$$

$$\left.+\frac{\exp(c^2\tau)\mathrm{erfc}(c\sqrt{\tau})}{c(c-a)(c-b)(c-d)}+\frac{\exp(d^2\tau)\mathrm{erfc}(d\sqrt{\tau})}{d(d-a)(d-b)(d-c)}\right].$$

Using the asymptotic expansion of eq. (6.41) we obtain,

$$(6.42)\qquad \lim_{\tau\to\infty}\psi(\tau)=2D_o\frac{\zeta}{K},$$

which is the same result as obtained in the Stokes limit. At this point we can make a remark about the validity of eqs. (6.37) and (6.38). With the data of Derksen [32] we obtain at room temperature: $\Delta_{max}\approx\sqrt{2D_o\zeta/K}\cong4\times10^{-8}<<R$. From eq. (6.42) we may conclude that a diffusion coefficient cannot be defined, although in case of $\zeta>>\sqrt{Km}$ a diffusion regime exists. As mentioned before we can distinguish two time scales. On the smaller the mean square displacement of the Brownian particle behaves like the one of the

free Brownian particle and diffusion like behaviour can be expected. At the larger time scale the effects of the harmonic potential become dominant and the mean square displacement tends to a constant value. These time scales have been discussed already in the context of the velocity autocorrelation function. In the Stokes limit diffusive behaviour can be shown over several decades of the Brownian time τ_B if $\zeta/\sqrt{Km} \geq 100$. This diffusive behaviour is shown by the expression $\psi(\tau) \approx 2D_o\tau$ for large τ, but τ small enough so that the correlation functions are not influenced by the harmonic potential. However, if we include backflow effects the system does not reach the diffusive regime unless $\zeta/\sqrt{Km} \geq 10^6$.

6.4 A Brownian particle in shear flow

We consider a shear flow in the x–direction with a velocity gradient in the z–direction and write

$$\underline{U}_o = (\lambda z,0,0)\,, \tag{6.43}$$

with λ the velocity gradient. We assume that λ is very small. The total fluid velocity field, composed of the shear flow and the fluid motion induced by the small Brownian particle, will then satisfy the linear Navier–Stokes equations. We do not consider rotational motion. San Miguel and Sancho solved this problem in the Stokes limit [33]. They showed the following long time behaviour of the position auto– and cross correlation functions respectively:

$$<x^2(t)> \simeq \tfrac{2}{3}D_o\lambda^2 t^3\,, \quad <y^2(t)> = <z^2(t)> = 2D_o t\,, \tag{6.44}$$

$$<x(t)z(t)> \simeq D_o\lambda t^2\,. \tag{6.45}$$

We see that the mean square displacement is proportional to t^3, assuming that at t=0 the particle is in the origin. Consequently there is no diffusive behaviour in the x–direction any longer. As can be expected isotropy has disappeared. This behaviour can be understood as follows: the rms displacement Δz is proportional to $\sqrt{t}$, which results in rms displacement in the x–direction proportional to $\lambda t\Delta z \simeq \lambda t\sqrt{t}$. The mean square displacement in the x–direction is then proportional to $\lambda^2 t^3$. Derksen has presented some results of experiments to measure this behaviour [32]. Bedeaux, Rubi and Pérez–Madrid have studied a similar problem including the non–linear term in the Navier–Stokes equations [34–36]. First they determined the friction tensor belonging to a spherical particle in a fluid with elongational flow. This friction tensor is modified by terms related to the rate of elongation. Consequently this modified friction tensor leads, via the fluctuation–dissipation theorem, to a modified version of the random force autocorrelation function. They have calculated the velocity correlation function and the mean square displacement of a Brownian particle in elongational flow [35], but in the diffusive regime only. They have not presented results for the convective regime. This section aims at the determination of these functions in the convective regime for simple shear flow, but under such conditions that we can linearize the Navier–Stokes equations. This is possible because we linearize these equations in the perturbation of the fluid velocity, caused by the moving particle, and furthermore we see that $(\underline{U}_o \cdot \nabla)\underline{U}_o = \underline{0}$ (eq. (6.43)). Consequently the friction tensor remains unchanged [34].

We now present the results of a study of this problem, where we have used a Stokes–Boussinesq like equation of motion. Using the generalized Faxén theorem, derived by Bedeaux and Mazur [26], we can derive the following equation of motion of a Brownian particle in shear flow:

$$M\dot{U}_x(t) = -6\pi\eta_o a U_x(t) - 6a^2\sqrt{\pi\rho\eta_o}\int_0^t \frac{1}{\sqrt{t-\tau}}\,\dot{U}_x(\tau)\,d\tau \qquad (6.46)$$

$$+ \lambda\left[6\pi\eta_o a z(t) + 6a^2\sqrt{\pi\rho\eta_o}\int_0^t \frac{1}{\sqrt{t-\tau}}\, U_z(\tau)d\tau + \tfrac{3}{2}m_0 U_z(t)\right] + R_x(t)\,,$$

$$(6.47) \qquad M\dot{U}_z(t) = -6\pi\eta_o a U_z(t) - 6a^2\sqrt{\pi\rho\eta_o}\int_0^t \frac{1}{\sqrt{t-\tau}}\, \dot{U}_z(\tau)d\tau + R_z(t)\,,$$

In the y–direction the problem can be described by using the results of the free Brownian particle presented in section 2. We assume that $\underline{U}(t)=\underline{0}$ if $t\leq 0$. We present the results for the mean square displacement only. To obtain that quantity we solve this set of equations by studying the Laplace transforms of both equations, which are,

$$(6.48) \qquad \tilde{x}(s) = \tilde{B}(s)\tilde{D}(s)\tilde{z}(s) + \tilde{B}(s)\tilde{R}_x(s)\,,$$

$$(6.49) \qquad \tilde{z}(s) = \tilde{B}(s)\tilde{R}_z(s)\,,$$

where,

$$(6.50) \qquad \tilde{B}(s) = \frac{1}{s(Ms + z\sqrt{s} + \zeta)}\,, \quad \tilde{D}(s) = \lambda(\zeta + z\sqrt{s} + \tfrac{3}{2}m_0 s)$$

The solution of the mean square displacement in the z–direction has already been presented in section 2 (eq. (6.26)). Substitution of eq. (6.49) for $\tilde{z}(s)$ in eq. (6.48) gives

$$(6.51) \qquad x(s) = \tilde{B}^2(s)\tilde{D}(s)\tilde{R}_z(s) + \tilde{B}(s)\tilde{R}_x(s)$$

The position autocorrelation function $\langle\tilde{x}(s)\tilde{x}(s')\rangle$ now becomes,

$$(6.52) \qquad \langle\tilde{x}(s)\tilde{x}(s')\rangle = \langle\tilde{x}(s)\tilde{x}(s')\rangle_\lambda + \tilde{B}(s)\tilde{B}(s')\langle\tilde{R}_x(s)\tilde{R}_x(s')\rangle\,,$$

where the last part of this equation is again a contribution already known from section 2. The term $<\tilde{x}(s)\tilde{x}(s')>_\lambda$ is the pure shear contribution and has the form

$$(6.53) \qquad <\tilde{x}(s)\tilde{x}(s')>_\lambda = \tilde{B}_\lambda(s)\tilde{B}_\lambda(s')<\tilde{R}_z(s)\tilde{R}_z(s')> ,$$

with $\tilde{B}_\lambda(s)=\tilde{B}^2(s)\tilde{D}(s)$. In the derivation of eq. (6.52) we have used the property of the random forces that cross correlations are zero [26]. Furthermore the following position cross correlation function can be determined,

$$(6.54) \qquad <\tilde{x}(s)\tilde{z}(s')> = <\tilde{x}(s)\tilde{z}(s')>_\lambda = \tilde{B}_\lambda(s)\tilde{B}(s')<\tilde{R}_z(s)\tilde{R}_z(s')> .$$

We know (see section 2 eq. (6.16)) that

$$(6.55) \qquad <\tilde{R}_z(s)\tilde{R}_z(s')> = \frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} .$$

Furthermore we can derive,

$$(6.56) \qquad \tilde{B}_\lambda(s)\tilde{\theta}(s) = k_B T(\tilde{C}_\lambda(s) - Ms\tilde{B}_\lambda(s)) , \quad \tilde{C}_\lambda(s) = \tilde{B}(s)\tilde{D}(s)/s$$

With both results we come to the following relation describing the shear flow depending part of the Laplace transform of the position autocorrelation function:

$$(6.57) \qquad <\tilde{x}(s)\tilde{x}(s')>_\lambda = k_B T\left[\frac{\tilde{B}_\lambda(s)\tilde{C}_\lambda(s') + \tilde{B}_\lambda(s')\tilde{C}_\lambda(s)}{s+s'} - M\tilde{B}_\lambda(s)\tilde{B}_\lambda(s')\right] .$$

To derive the inverse Laplace transform we refer again to the review article of Fox (ref.[27] p. 195). In line with the derivation shown there to calculate a double Laplace transform we

obtain,

$$(6.58)\qquad \int_0^\infty dt_1 \int_0^\infty dt_2 \exp(-st_1)\exp(-s't_2) \int_0^{t_2} d\tau_2 \int_0^{t_1} d\tau_1 f(t_1-\tau_1)g(t_2-\tau_2)\delta(|\tau_2-\tau_1|)$$

$$= \int_0^\infty dt_2 \int_0^\infty dt_1 \exp(-st_1)\exp(-s't_2) \int_0^{t_1} f(t)g(t+\tau)dt = \frac{\tilde{f}(s)\tilde{g}(s')}{s+s'},$$

where we assume that $\tau=t_2-t_1\geq 0$. The function $\delta(t)$ is the Dirac delta function. The inverse Laplace transform of eq. (6.57) is now,

(6.59)

$$<x(t_1)x(t_2)>_\lambda = k_B T\left[\int_0^{t_1} B_\lambda(t)C_\lambda(t+\tau)dt + \int_0^{t_1} B_\lambda(t+\tau)C_\lambda(t)dt - MB_\lambda(t_1)B_\lambda(t_2)\right].$$

In an analogous way the Laplace transform of the position cross correlation function becomes

$$(6.60)\qquad <\tilde{x}(s)\tilde{z}(s')>_\lambda = k_B T\left[\frac{(\tilde{B}_\lambda(s)/s') + \tilde{C}_\lambda(s)\tilde{B}(s')}{s+s'} - M\tilde{B}_\lambda(s)\tilde{B}(s')\right].$$

Finally, Laplace inversion gives

$$(6.61)\quad <x(t_1)z(t_2)>_\lambda = k_B T\left[\int_0^{t_1} B_\lambda(t)dt + \int_0^{t_1} B(t+\tau)C_\lambda(t)dt - MB_\lambda(t_1)B(t_2)\right].$$

We have now derived some formal expressions for the position auto– and cross correlation functions, but must evaluate the functions $B(t)$, $B_\lambda(t)$ and $C_\lambda(t)$. We confine ourselves to an outline of these derivations only. They can be obtained with the help of tables of Laplace transforms [28]. We know (eq. (6.50)):

$$(6.62)\qquad \tilde{B}(s) = \frac{1}{s(Ms+z\sqrt{s}+\zeta)}$$

The inverse Laplace transform of $\tilde{B}(s)$ is

$$(6.63) \qquad B(t) = \frac{1}{\zeta}\left[1 + \frac{1}{(b-a)}\left[a\exp(b^2t)\mathrm{erfc}(b\sqrt{t}) - b\exp(a^2t)\mathrm{erfc}(a\sqrt{t})\right]\right],$$

with a and b defined below eq. (6.20). Again we assume for the moment that $a \neq b$. The function $\tilde{B}_\lambda(s)$ is defined as

$$(6.64) \qquad \tilde{B}_\lambda(s) = \tilde{B}^2(s)\tilde{D}(s) = \lambda\left[(\tilde{B}(s)/s) + (m_0-m)s\tilde{B}^2(s)\right].$$

Laplace inversion of the first part of eq. (6.64) gives, via $\tilde{B}(s)/s=\tilde{C}(s)$, the function C(t) which is presented in eq. (6.26) and the Laplace inverse of the second part of eq. (6.64) can be obtained using the convolution theorem. The final result is,

$$(6.65) \qquad B_\lambda(t) = \lambda\left[C(\tau) + (m_0-m)\int_0^t \frac{dB(\tau)}{d\tau} B(t-\tau)d\tau\right].$$

The function $\tilde{C}_\lambda(s)$ is defined as

$$(6.66) \qquad \tilde{C}_\lambda(s) = \tilde{B}(s)\tilde{D}(s)/s = \frac{\lambda}{s^2} + \lambda(m_0-m)\tilde{B}(s),$$

and the inverse Laplace transform is

$$(6.67) \qquad C_\lambda(t) = \lambda\left[t + (m_0-m)B(t)\right].$$

The position correlation functions can now be determined and the final results be evaluated both analytically and numerically, but we restrict ourselves to the long time behaviour of these correlation functions. If $t_1=t_2=t$ we have

$$(6.68) \qquad \langle x^2(t)\rangle_\lambda = k_B T\Big[2\int_0^t B_\lambda(\tau)C_\lambda(\tau)d\tau - MB_\lambda^2(t)\Big] ,$$

and

$$(6.69) \qquad \langle x(t)z(t)\rangle_\lambda = k_B T\Big[\int_0^t B_\lambda(\tau)d\tau + \int_0^t B(\tau)C_\lambda(\tau)d\tau - MB_\lambda(t)B(t)\Big] .$$

In the long time limit there is no need to evaluate the functions $B(t)$, $B_\lambda(t)$ and $C_\lambda(t)$ in detail. These functions can be rewritten as follows

$$(6.70) \qquad B(t) = \frac{1}{\zeta} - \frac{z}{\zeta^2\sqrt{\pi}}\frac{1}{\sqrt{t}} + B_1(t)$$

$$(6.71) \qquad B_\lambda(t) = \lambda\frac{t}{\zeta}\Big[1 - \frac{2z}{\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}} + \frac{1}{\zeta^2}(z^2 - M\zeta + (m_0 - m)\zeta)\frac{1}{t} + B_2(t)\Big]$$

$$(6.72) \qquad C_\lambda(t) = \lambda\frac{t}{\zeta}\Big[\zeta + (m_0 - m)\frac{1}{t} + C_1(t)\Big]$$

The long time behaviour is given by asymptotic expansions of $B_1(t)$, $B_2(t)$ and $C_1(t)$. The leading terms of these functions are $O(t^{-3/2})$. Substitution of these expressions for the functions $B(t)$, $B_\lambda(t)$ and $C_\lambda(t)$ in the eqs. (6.68) and (6.69) respectively gives the following expressions:

$$(6.73) \quad \langle x^2(t)\rangle_\lambda = \tfrac{2}{3}D_o\lambda^2 t^3\Big[1 - \frac{12z}{5\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}} + \frac{3}{2\zeta^2}(z^2 - 2M\zeta + 2(m_0 - m)\zeta)\frac{1}{t} + O(\frac{1}{t\sqrt{t}})\Big] ,$$

$$(6.74) \quad \langle x(t)z(t)\rangle_\lambda = D_o\lambda t^2\Big[1 - \frac{2z}{\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}} + \frac{1}{\zeta^2}(z^2 - 2M\zeta + 2(m_0 - m)\zeta)\frac{1}{t} + O(\frac{1}{t\sqrt{t}})\Big] .$$

These results can be compared with the expressions obtained by San Miguel and Sancho

[33], which are the expressions above in the Stokes limit,

$$(6.75) \qquad \langle x^2(t)\rangle_\lambda = \tfrac{2}{3} D_o \lambda^2 t^3 \left[1 - \frac{6m}{\zeta}\frac{1}{t} + O(t^{-2})\right]$$

$$(6.76) \qquad \langle x(t)z(t)\rangle_\lambda = D_o \lambda t^2 \left[1 - \frac{4m}{\zeta}\frac{1}{t} + O(t^{-2})\right]$$

These relations can also be obtained by taking the limits $m_0 \to 0$ and $z \to 0$ in eqs. (6.73) and (6.74). It is clear that no diffusional regime on these time scales exists. Furthermore we can estimate the value of τ_B for which the expressions of $\langle x^2(t)\rangle_\lambda$ become nearly cubic in time. In the Stokes limit this will take place if $\tau_B \approx O(10^4)$, but by including backflow effects we reach this point if $\tau_B \approx O(10^7)$. Finally we want to point out that the term proportional to t^2 in eq. (6.73) (or the term proportional to t in eq. (6.74)) disappears if $\sigma = \frac{11}{8}$ in contrast with the results obtained by San Miguel and Sancho (eqs. (6.75) and (6.76)).

It is also possible to study a combination of both situations described in the sections 3 and 4, a Brownian particle in a harmonic potential and in shear flow. In the Stokes limit some results are available, obtained by van den Broeck, Sancho and San Miguel [37]. With the methods presented in this chapter it is possible to include backflow effects in such a problem. However, we refrain from such calculation because of the disproportion between the mathematical complexity and the modesty of new insights gained.

6.5 Conclusion

We have been able to extend the theory of Brownian motion, including backflow effects, to the case of a Brownian particle in a harmonic potential and of a Brownian particle in an externally imposed shear flow. An significant point is that these two problems can be studied by using the same mathematical tools as used for the free

Brownian particle problem. These tools are also be useful for the study of a Brownian particle in a combined shear flow and harmonic potential, although we have not demonstrated this explicitly. An important conclusion from this chapter is that the mean square displacement, determined with the Stokes–Boussinesq equation of motion, differs considerably from the same function obtained in the Stokes limit, up to large values of the dimensionless time τ_B. We have seen that a Brownian particle in a harmonic potential, described in section 3, cannot reach the diffusive regime, while in the Stokes limit this diffusive regime is reached in otherwise comparable circumstances. We can also see that the velocity autocorrelation function of a particle in a harmonic potential shows long time tail behaviour, although the algebraic power of this tail is lower in comparison to the free particle case, viz. $t^{-7/2}$ versus $t^{-3/2}$. In the case of shear flow the leading asymptotic terms of the mean square displacement functions are the same as in the Stokes limit. Other terms are quite different, however. Even more significant is the fact that the relaxation time in which the asymptotic regime is reached, is much longer if backflow effects are taken into account.

In this chapter we have neglected hydrodynamic interactions. These become only important if the volume fraction of dispersed Brownian particles becomes large. In the next chapter we shall present the results of a study of the influence of retarded hydrodynamic interactions on transport coefficients of suspensions.

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Chapter 7 RETARDED HYDRODYNAMIC INTERACTIONS IN SUSPENSIONS

7.1 Introduction

In chapter 2 we presented a method to calculate the components of the grand mobility matrix of a system of N spherical particles in an unbounded fluid with an externally imposed flow. In that chapter we assumed that the fluid velocity changes slowly, so that the local time derivative may be neglected. This chapter is dedicated to the solution of the Navier–Stokes equation for a system of two particles in an unbounded fluid including time dependent effects. With this solution we can study the effects of the retarded hydrodynamic interactions on the behaviour of dilute suspensions. If we want to study more concentrated suspensions we have to include three and more particle interactions in the calculations of the grand mobility matrix.

What is the reason to study the effects of the retarded hydrodynamic interactions on the behaviour of suspensions? The most important reason is the expectation that the retardation effects caused by a moving particle will influence neighbouring particles especially if the interparticle distances are small. We expect that these effects are significant for concentrated suspensions, and that these retarded hydrodynamic interactions will influence the behaviour of the velocity auto– and cross correlation functions of Brownian particles. These correlation functions are not changed only at time scales comparable with the relaxation time of the velocities of the Brownian particles, as can be expected, but also at larger time scales. This can be shown with the existence of long time tails in the correlation functions. Even in the case of a single spherical particle in an unbounded fluid we can demonstrate that the retardation effects influence the velocity

autocorrelation function. We can show this with the example of a spherical particle moving with velocity $\underline{U}(t)$ in an unbounded incompressible fluid at rest at infinity. Assuming that we can use the linearized incompressible time dependent Navier–Stokes equations (later abbreviated as N.S. equations) we shall describe the hydrodynamic force exerted by the fluid on the particle by the so called Stokes–Boussinesq equation [1, 2]

$$\underline{F}(t) = -6\pi\eta_o a\underline{U}(t) - \tfrac{1}{2}m_0\frac{d\underline{U}(t)}{dt} - 6a^2\sqrt{\pi\rho\eta_o}\int_{-\infty}^{t}\frac{1}{\sqrt{t-\tau}}\frac{d\underline{U}(\tau)}{d\tau}\,d\tau\,, \tag{7.1}$$

with

ρ: the density of the fluid ,

η_o: the shear viscosity of the fluid ,

a: the radius of the particle ,

$m_0 = \frac{4}{3}\pi a^3\rho$.

The first term of eq. (7.1) is the ordinary Stokes' friction, the second is connected with the virtual mass of a sphere in an incompressible fluid, and the third is a memory term associated with the hydrodynamic retardation effects and related to the penetration depth of viscous unsteady flow around a sphere. We are particularly interested in this memory term. If the sphere has a nonconstant velocity $\underline{U}(t)$ it will affect the fluid velocity in the neighbourhood of the sphere and the fluid in its turn will, a time Δt later on, affect the velocity of the sphere. It is not difficult to see that in case there is a second particle in the neighbourhood of the first particle the disturbance of the fluid velocity caused by the first particle will affect a time Δt later on the velocity of the second particle and vice versa. With the help of eq. (7.1) we can calculate the velocity autocorrelation function of a spherical particle in an unbounded fluid and the result shows the famous $t^{-3/2}$ long time tail [3] and with the help of the velocity autocorrelation function $\phi(t)$ we can define the time dependent diffusion coefficient D(t):

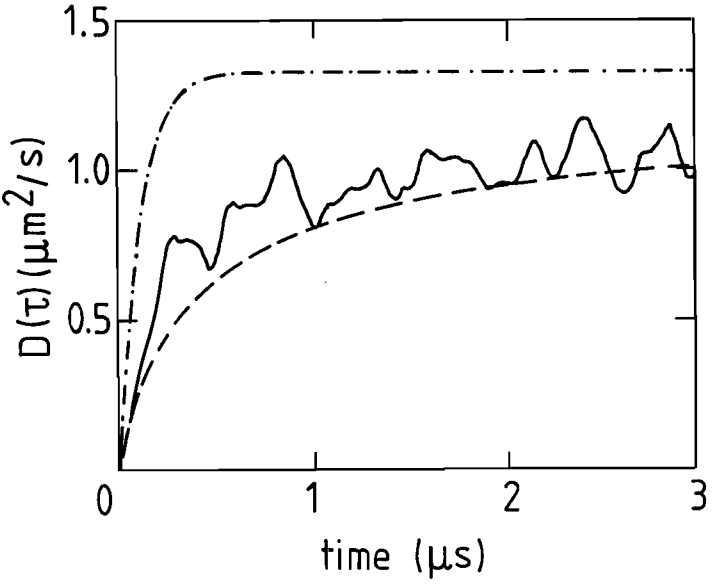

Fig.1. *Time dependent diffusion coefficient as measured by Weitz et al.. Solid line: experiment; dash–dotted line: theory without retardation effects (Stokes limit); dashed line: theory including retardation effects.*

$$D(t) \equiv \int_0^t \phi(t')dt' , \qquad (7.2)$$

with: $\lim_{t\to\infty} D(t) = D_o$, the Stokes–Einstein diffusion coefficient. Recently Weitz et al. have measured D(t) and confirmed the existence of the retardation effects (see fig.1) [4]. Finally we emphasize another important reason to study the retarded hydrodynamic interactions. If we do not include the retardation effects we are not always able to calculate configurationally averaged quantities, i.e. averages of quantities such as velocity correlation functions over all possible configurations of the Brownian particles, because of divergencies. Inclusion of the retardation effects removes some divergencies, but introduces some

conditionally convergent integrals. A carefull treatment then enables us to calculate the averages.

In section 2 we introduce the set of basic solutions, in section 3 we show how one can calculate the set of linear equations of the coefficients, in section 4 we express the force and torque exerted by the fluid on the particles in terms of some coefficients, in section 5 we derive the correlation matrix and in the sections 6 and 7 we present some results.

7.2 The basic solutions

We look at a system of two spherical particles immersed in an unbounded incompressible fluid. The fluid is at rest at infinity. The spherical particles have velocities $\underline{U}_1(t)$ and $\underline{U}_2(t)$ and rotational velocities $\underline{\Omega}_1(t)$ and $\underline{\Omega}_2(t)$ respectively. The radii of both particles are the same, $a_1=a_2=a$, and the interparticle distance is R. The interparticle axis is the z–axis of our problem. The fluid velocity satisfies the N.S. equations:

$$\eta_o \nabla^2 \underline{v}(\underline{r},t) - \nabla p(\underline{r},t) = \rho \frac{\partial \underline{v}(\underline{r},t)}{\partial t}, \tag{7.3}$$

$$\nabla \cdot \underline{v}(\underline{r},t) = 0, \tag{7.4}$$

where $\underline{v}(\underline{r},t)$ is the fluid velocity and $p(\underline{r},t)$ is the pressure at time t, η_o is the shear viscosity and ρ is the density of the fluid. These N.S. equations can be simplified by introducing the Fourier transforms

$$\underline{v}(\underline{r},t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \underline{v}(\underline{r},\omega)e^{-i\omega t}d\omega, \quad p(\underline{r},t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} p(\underline{r},\omega)e^{-i\omega t}d\omega. \tag{7.5}$$

The Fourier transformed N.S. equations (7.3) and (7.4) are now

$$\eta_o \nabla^2 \underline{v}(\underline{r},\omega) - \nabla p(\underline{r},\omega) = \eta_o \alpha^2 \underline{v}(\underline{r},\omega) \,, \tag{7.6}$$

$$\nabla \cdot \underline{v}(\underline{r},\omega) = 0 \,, \tag{7.7}$$

with $\alpha = \sqrt{-i\omega\rho/\eta_o}$, $\mathrm{Re}(\alpha) \geq 0$. To solve the N.S. equations we need the boundary conditions at the surfaces of both particles. We suppose stick boundary conditions which can be stated in the following way:

$$\underline{v}(\underline{r},\omega) = \underline{U}_i(\omega) + \underline{\Omega}_i(\omega) \times (\underline{r} - \underline{R}_i) \quad \text{with:} \underline{r} \in S_i,\ i=1,2 \,, \tag{7.8}$$

where S_i is the surface of particle i. We further suppose that we look at such short time scales that the configuration of the two particles does not change significantly. In that case $\underline{R}_i$ is not a function of ω. See e.g. the short discussion and the references quoted in section 2.2. If we have determined $\underline{v}(\underline{r},\omega)$ and $p(\underline{r},\omega)$ we are able to determine the force $\underline{F}_i(\omega)$ and torque $\underline{T}_i(\omega)$ exerted by the fluid on the particles. In the case of spherical particles:

$$\underline{F}_i(\omega) = -a^2 \int_{|\underline{r}_i|=a} \underline{\Pi}_r(\underline{r}_i,\omega) d\Omega_i \,, \quad \underline{T}_i(\omega) = -a^3 \int_{|\underline{r}_i|=a} (\hat{e}_r \times \underline{\Pi}_r(\underline{r}_i,\omega)) d\Omega_i \,, \tag{7.9}$$

with $d\Omega$ the element of solid angle, $\hat{e}_r$ the radial unit vector in a spherical coordinate system and

$$\underline{\Pi}_r(\underline{r},\omega) = p(\underline{r},\omega)\hat{e}_r - \eta_o \left[\frac{\partial}{\partial r} - \frac{1}{r}\right] \underline{v}(\underline{r},\omega) - \frac{\eta_o}{r} \nabla (\underline{r} \cdot \underline{v}(\underline{r},\omega)) \,. \tag{7.10}$$

In the same way as in chapter 2, we define the grand mobility matrix for a two particle system:

$$\begin{bmatrix} \underline{U}(\omega) \\ \underline{\Omega}(\omega) \end{bmatrix} = - \begin{bmatrix} \mu^{tt}(\omega) & \mu^{tr}(\omega) \\ \mu^{rt}(\omega) & \mu^{rr}(\omega) \end{bmatrix} \cdot \begin{bmatrix} \underline{F}(\omega) \\ \underline{T}(\omega) \end{bmatrix} \,, \quad \text{with } \underline{U}(\omega) = \begin{bmatrix} \underline{U}_1(\omega) \\ \underline{U}_2(\omega) \end{bmatrix} \text{ etc.} \tag{7.11}$$

The grand resistance matrix is the inverse of the grand mobility matrix. Finally we want to note that the symmetry relations (eq. (2.13)) are still valid.

The complete set of basic solutions of the N.S. equations which we shall use in the two particle problem has already been formulated by Felderhof and Jones [5]. They formulated their set of basic solutions, which is convenient for the problem of a spherical particle in an unbounded fluid, in the case of the one particle problem. One of the basic ingredients of the set of basic solutions is the set of vector spherical harmonics $\underline{A}_{lm}(\theta,\varphi)$, $\underline{B}_{lm}(\theta,\varphi)$ and $\underline{C}_{lm}(\theta,\varphi)$. In chapter 2 section 3 we paid much attention to the vector spherical harmonics. Other important ingredients are the "solid spherical harmonics" as defined by Felderhof and Jones. They have the following form:

$$(7.12)\quad \phi^{+}_{lm}(\underline{r}) = r^{l}Y_{lm}(\theta,\varphi)\,, \qquad \phi^{-}_{lm}(\underline{r}) = r^{-(l+1)}Y_{lm}(\theta,\varphi)\,,$$

$$(7.13)\quad \Psi^{+}_{lm}(\underline{r}) = g_{l}(\alpha r)Y_{lm}(\theta,\varphi)\,, \qquad \Psi^{-}_{lm}(\underline{r}) = k_{l}(\alpha r)Y_{lm}(\theta,\varphi)\,,$$

with $Y_{lm}(\theta,\varphi)$ the spherical harmonics. The functions $g_{l}(\alpha r)$ and $k_{l}(\alpha r)$ are the modified spherical Bessel functions with [6]

$$g_{l}(\alpha r) = \sqrt{\pi/(2\alpha r)}\, I_{l+\frac{1}{2}}(\alpha r)\,, \qquad k_{l}(\alpha r) = \sqrt{\pi/(2\alpha r)}\, K_{l+\frac{1}{2}}(\alpha r)\,.$$

The set of basic solutions, which behave regularly for $|\underline{r}|\to\infty$, in the case of a spherical particle with center in the origin O is now

$$(7.14a)\qquad \underline{v}_{lm\alpha}(\underline{r},\omega) = \frac{-1}{\alpha^{2}(2l+1)}\nabla\phi^{-}_{lm}(\underline{r}) = \frac{-r^{-(l+2)}}{\alpha^{2}(2l+1)}\underline{B}_{lm}(\theta,\varphi)\,,$$

$$(7.14b)\qquad \underline{v}_{lm\beta}(\underline{r},\omega) = \frac{2\alpha}{\pi l(l+1)}(\nabla\times\underline{r}\psi^{-}_{lm}(\underline{r})) = \frac{2\alpha}{\pi l(l+1)}k_{l}(\alpha r)\underline{C}_{lm}(\theta,\varphi)\,,$$

$$(7.14c)\qquad \underline{v}_{lm\gamma}(\underline{r},\omega) = \frac{-2\alpha}{\pi l(l+1)}\left(\frac{\nabla\times(\nabla\times\underline{r}\psi^{-}_{lm}(\underline{r}))}{\alpha}\right)$$

$$= \frac{2\alpha}{\pi l(l+1)(2l+1)}\left((l+1)k_{l-1}(\alpha r)\underline{A}_{lm}(\theta,\varphi) + lk_{l+1}(\alpha r)\underline{B}_{lm}(\theta,\varphi)\right) .$$

The indices l and m satisfy the condition that $l \geq 1$ and $m \leq |l|$. We see that we have divergencies if we look at the limit $\alpha \to 0$. For a discussion about this point and the differences between this set of basic solutions and the set of basic solutions presented in chapter 2, we refer to the article by Felderhof and Jones [5]. The accompanying basic solutions for the pressure $p(\underline{r},\omega)$ are

$$(7.15)\qquad p_{lm\alpha}(\underline{r},\omega) = \frac{\eta_o}{2l+1} r^{-(l+1)} Y_{lm}(\theta,\varphi) , \quad p_{lm\beta}(\underline{r},\omega) = p_{lm\gamma}(\underline{r},\omega) = 0 .$$

With the help of the linearity of the N.S. equations, we can now express the fluid velocity $\underline{v}(\underline{r},\omega)$ and the pressure $p(\underline{r},\omega)$ as a superposition of basic solutions:

$$(7.16)\qquad \underline{v}(\underline{r},\omega) = \sum_{\substack{l\geq 1 \\ m}} \left[\alpha_{lm}(\omega)\underline{v}_{lm\alpha}(\underline{r},\omega) + \beta_{lm}(\omega)\underline{v}_{lm\beta}(\underline{r},\omega) + \gamma_{lm}(\omega)\underline{v}_{lm\gamma}(\underline{r},\omega)\right] ,$$

$$(7.17)\qquad p(\underline{r},\omega) = \sum_{\substack{l\geq 1 \\ m}} \alpha_{lm}(\omega) p_{lm\alpha}(\underline{r},\omega) ,$$

where the summation runs over all the allowed values of the indices l and m.

7.3 The set of linear equations

The N.S. equations are linear equations and for that reason we can rewrite the fluid velocity $\underline{v}(\underline{r},\omega)$ with the help of two velocity fields, one defined with respect to the center of particle 1 and the other defined with respect to the center of particle 2. The result is

$$\underline{v}(\underline{r},\omega) = \underline{v}_1(\underline{r}_1,\omega) + \underline{v}_2(\underline{r}_2,\omega) \quad \text{with: } \underline{r}_i = \underline{r}-\underline{R}_i,\ i=1,2\ . \tag{7.18}$$

In terms of basic solutions,

$$\underline{v}(\underline{r},\omega) = \sum_{i=1}^{2} \sum_{\substack{l\geq 1 \\ m}} \left[\alpha^i_{lm}(\omega)\underline{v}_{lm\alpha}(\underline{r}_i,\omega) + \beta^i_{lm}(\omega)\underline{v}_{lm\beta}(\underline{r}_i,\omega) + \gamma^i_{lm}(\omega)\underline{v}_{lm\gamma}(\underline{r}_i,\omega) \right] . \tag{7.19}$$

If we want to use the method of chapter 2 to determine the set of linear equations of the coefficients $\{\alpha^i_{lm}(\omega),\beta^i_{lm}(\omega),\gamma^i_{lm}(\omega)\}$ we must express the fluid velocity $\underline{v}(\underline{r},\omega)$ with respect to the center of particle 1, origin O_1, and the center of particle 2, origin O_2 respectively. As a consequence we have to express the basic solutions defined with respect to the origin O_2 in terms of basic solutions defined with respect to the origin O_1 and vice versa. If we take into account the special configuration of the particles then this is possible by using the Hobson formula [7] and a generalized Hobson formula. The Hobson formula expresses the solid spherical harmonic $\phi^-_{lm}(\underline{r}_2)$ in terms of the solid spherical harmonics $\phi^+_{lm}(\underline{r}_1)$ and vice versa:

$$\phi^-_{lm}(\underline{r}_j) = \sum_{\substack{s\geq 0 \\ t}} \frac{n_{st}}{(s+t)!} M^{ji}_{lm;st}(R)\phi^+_{st}(\underline{r}_i) \quad , |\underline{r}_i|<R \text{ and } i,j\in\{1,2\} . \tag{7.20}$$

with the $M^{ji}_{lm;st}(R)$ defined in eqs. (3.2) and (3.3) and n_{lm} defined in eq. (2.34). The generalized Hobson formula expresses the "solid spherical harmonic" $\psi^-_{lm}(\underline{r}_2)$ in terms of the "solid spherical harmonics" $\psi^+_{lm}(\underline{r}_1)$ and vice versa. These expressions are derived in

appendix III and the shorthand notations are

$$(7.21)\qquad \psi^{-}_{lm}(\underline{r}_j) = \sum_{s\geq 0}(-1)^s[N^m(\alpha R)]^{ji}_{ls}\psi^{+}_{sm}(\underline{r}_i)\,, \quad |\underline{r}_i|<R \text{ and } i,j\in\{1,2\}\,,$$

with

$$[N^m(\alpha R)]^{21}_{ls} = \sum_{p\geq 0}(-1)^p(2p+1)k_p(\alpha R)[P_p(M^m)]_{ls}\,,\quad [N^m(\alpha R)]^{12}_{ls} = (-1)^{l+s}[N^m(\alpha R)]^{21}_{ls}\,,$$

where P_p is a Legendre polynomial. For a discussion on the matrices $[N^m(\alpha R)]^{ji}$ see also appendix III. Rewriting the fluid velocity $\underline{v}(\underline{r},\omega)$ we obtain $\underline{v}^i(\underline{r}_i,\omega)$, the fluid velocity with respect to the origin O_i:

$$(7.22)\quad \underline{v}^i(\underline{r}_i,\omega) = \sum_{\substack{l\geq 1\\ m}}\Bigg[\frac{-1}{\alpha^2(2l+1)}\alpha^i_{lm}(\omega)r_i^{-(l+2)}\underline{B}_{lm}(\theta_i,\varphi_i) + \frac{2\alpha}{\pi l(l+1)}\beta^i_{lm}(\omega)k_l(\alpha r_i)\underline{C}_{lm}(\theta_i,\varphi_i)$$

$$+\frac{2\alpha}{\pi l(l+1)(2l+1)}\gamma^i_{lm}(\omega)\Big[(l+1)k_{l-1}(\alpha r_i)\underline{A}_{lm}(\theta_i,\varphi_i) + lk_{l+1}(\alpha r_i)\underline{B}_{lm}(\theta_i,\varphi_i)\Big]$$

$$+\sum_{s\geq 0}\Bigg[\frac{-1}{\alpha^2(2l+1)}\alpha^j_{sm}(\omega)\frac{n_{sm}}{(s+m)!}M^{ji}_{lm;sm}(R)r_i^{s-1}\underline{A}_{sm}(\theta_i,\varphi_i) + \frac{2\alpha}{\pi l(l+1)}\beta^j_{sm}(\omega)[N^m(\alpha R)]^{ji}_{ls}$$

$$\times\Big[g_s(\alpha r_i)\underline{C}_{sm}(\theta_i,\varphi_i) + \frac{\alpha}{2s+1}\Big[g_{s-1}(\alpha r_i)\underline{A}_{sm}(\theta_i,\varphi_i) - g_{s+1}(\alpha r_i)\underline{B}_{sm}(\theta_i,\varphi_i)\Big]\times\underline{R}_{ij}\Big]$$

$$-\frac{2}{\pi l(l+1)}\gamma^j_{sm}(\omega)[N^m(\alpha R)]^{ji}_{ls}\Big[\underline{X}_{sm}(\underline{r}_i,\omega) + \alpha(\underline{R}_{ij}\cdot\hat{e}_z)\underline{Z}_{sm}(\underline{r}_i,\omega)\Big]\Bigg]\Bigg]\,,$$

where $\underline{R}_{12} = R\hat{e}_z$, $\underline{R}_{21} = -R\hat{e}_z$ and $\hat{e}_z$ is the unit vector in a Cartesian coordinate system. The vector functions $\underline{X}_{sm}(\underline{r},\omega)$ and $\underline{Z}_{sm}(\underline{r},\omega)$ are shorthand notations for long expressions. We give an outline of the derivation of these vector functions in appendix III. In an analogous way we can derive the following expression for $p^i(\underline{r}_i,\omega)$:

$$p^i(\underline{r}_i,\omega) = \sum_{\substack{l\geq 1\\ m}} \frac{\eta_o}{2l+1}\Bigg[\alpha^i_{lm}(\omega) r_i^{-(l+1)} Y_{lm}(\theta_i,\varphi_i) + \sum_{s\geq 0} \alpha^j_{sm}(\omega)\frac{n^{s\,m}}{(s+m)!} M^{j\,i}_{lm;sm}(R) r_i^s Y_{sm}(\theta_i,\varphi_i)\Bigg] . \tag{7.23}$$

To determine the relation between all the coefficients $\alpha^i_{lm}(\omega)$, $\beta^i_{lm}(\omega)$ and $\gamma^i_{lm}(\omega)$ on the one hand and the velocities $\underline{U}_i(\omega)$ and rotational velocities $\underline{\Omega}_i(\omega)$ on the other it is necessary to calculate the following inner products:

$$\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot \underline{A}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i , \tag{7.24}$$

$$\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot \underline{B}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i , \tag{7.25}$$

$$\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot \underline{C}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i . \tag{7.26}$$

We have to calculate these inner products for $\forall p\geq 1$, $|q|\leq p$ and i=1,2. These integrals are not difficult to work out because we can use the boundary conditions at the surfaces of the spheres. We have the same boundary conditions as used in chapter 2 and therefore we can use the eqs. (2.44)–(2.46) with the velocities and angular velocities as functions of ω,

$$\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot \underline{A}^*_{pq}(\theta_i,\varphi_i)\,d\Omega_i = \tfrac{3}{2}\delta_{p,1}\Big[n_{11}\big[\delta_{q,-1}-\delta_{q,1}\big]U_{ix}(\omega)+in_{11}\big[\delta_{q,-1}+\delta_{q,1}\big]U_{iy}(\omega)+2n_{10}\delta_{q,0}U_{iz}(\omega)\Big] , \tag{7.27}$$

$$(7.28)\qquad \int_{|\underline{r}_i|=a} \underline{v}^{\,i}(\underline{r}_i,\omega)\cdot\underline{B}^{*}_{pq}(\theta_i,\varphi_i)\,d\Omega_i = 0\,,$$

$$(7.29)\qquad \int_{|\underline{r}_i|=a} \underline{v}^{\,i}(\underline{r}_i,\omega)\cdot\underline{C}^{*}_{pq}(\theta_i,\varphi_i)\,d\Omega_i =$$

$$a\delta_{p,1}\left[n_{11}\left[\delta_{q,-1}-\delta_{q,1}\right]\Omega_{ix}(\omega)+in_{11}\left[\delta_{q,-1}+\delta_{q,1}\right]\Omega_{iy}(\omega)+2n_{10}\delta_{q,0}\Omega_{iz}(\omega)\right].$$

where we put the expansion coefficients, belonging to the externally imposed flow, equal to zero because we have assumed that the fluid is at rest at infinity. On the other hand we can substitute the r.h.s. of eq. (7.22) for $\underline{v}^{i}(\underline{r}_i,\omega)$ into the eqs. (7.24)–(7.26). We do not calculate the inner products explicitly but we refer the interested reader to appendix IV where we have tabulated most of the integrals necessary to determine the inner products. With the help of the following shorthand notations

$$(7.30)\qquad [X^q(\alpha R)]^{21}_{lp} \equiv (-1)^{l+1}\frac{2\alpha}{\pi l(l+1)}\Big[p(p+1)[N^q(\alpha R)]^{21}_{lp} +$$

$$\alpha R\frac{(p+q+1)p}{(2p+3)}\frac{n_{pq}}{n_{p+1,q}}[N^q(\alpha R)]^{21}_{l,p+1} - \alpha R\frac{(p+1)(p+q)}{(2p+1)}\frac{n_{p-1,q}}{n_{pq}}[N^q(\alpha R)]^{21}_{l,p-1}\Big]\,,$$

$$(7.31)\qquad [X^q(\alpha R)]^{12}_{lp} \equiv (-1)^{l+1}\frac{2\alpha}{\pi l(l+1)}\Big[p(p+1)[N^q(\alpha R)]^{12}_{lp} -$$

$$\alpha R\frac{(p+q+1)p}{(2p+3)}\frac{n_{pq}}{n_{p+1,q}}[N^q(\alpha R)]^{12}_{l,p+1} + \alpha R\frac{(p+1)(p+q)}{(2p+1)}\frac{n_{p-1,q}}{n_{pq}}[N^q(\alpha R)]^{12}_{l,p-1}\Big]\,,$$

$$(7.32)\qquad [Y^q(\alpha R)]^{21}_{lp} \equiv (-1)^{l}\frac{2iq\alpha^2 R}{\pi l(l+1)}[N^q(\alpha R)]^{21}_{lp}\,,$$

$$(7.33)\qquad [Y^q(\alpha R)]^{12}_{lp} \equiv (-1)^{l+1}\frac{2iq\alpha^2 R}{\pi l(l+1)}[N^q(\alpha R)]^{12}_{lp}\,,$$

$$(7.34) \qquad (Z^q)_{lp} \equiv \frac{-p(2p+1)}{\alpha^2(2l+1)} \frac{n_{pq}}{(p+q)!},$$

we can derive the following set of linear equations:

$$(7.35) \qquad \int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = \frac{2\alpha}{\pi} k_{p-1}(\alpha a)\gamma^i_{pq}(\omega)$$

$$+ a^{p-1}\sum_{l\geq 1}(Z^q)_{lp} M^{ji}_{lq;pq}(R)\alpha^j_{pq}(\omega) + g_{p-1}(\alpha a)\sum_{l\geq 1}\left[[Y^q(\alpha R)]^{ji}_{lp}\beta^j_{lq}(\omega) + [X^q(\alpha R)]^{ji}_{lp}\gamma^j_{lq}(\omega)\right],$$

$$(7.36) \qquad \int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot\underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = -\frac{(p+1)}{\alpha^2 a^{p+2}}\alpha^i_{pq}(\omega) + \frac{2\alpha}{\pi} k_{p+1}(\alpha a)\gamma^i_{pq}(\omega)$$

$$+ g_{p+1}(\alpha a)\sum_{l\geq 1}\left[[Y^q(\alpha R)]^{ji}_{lp}\beta^j_{lq}(\omega) + [X^q(\alpha R)]^{ji}_{lp}\gamma^j_{lq}(\omega)\right],$$

$$(7.37) \qquad \int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = \frac{2\alpha}{\pi} k_p(\alpha a)\beta^i_{pq}(\omega)$$

$$+ g_p(\alpha a)\sum_{l\geq 1}\left[[Y^q(\alpha R)]^{ji}_{lp}\gamma^j_{lq}(\omega) + [X^q(\alpha R)]^{ji}_{lp}\beta^j_{lq}(\omega)\right].$$

For al these equations: $p\geq 1$, $|q|\leq p$. If i=1 then j=2 and vice versa.

The presented infinite set of linear equations can be used to determine the grand mobility matrix. To attain this aim we have to introduce an upper limit for the allowed values of the indices l and p, i.e. $l_{max} = p_{max} = L$. With this restriction we assume that all the coefficients $\alpha^i_{lm}(\omega)$, $\beta^i_{lm}(\omega)$ and $\gamma^i_{lm}(\omega)$ are zero for $l>L$ and as a consequence we have created a finite set of linear equations and the solution of the coefficients $\alpha^i_{lm}(\omega)$ etc. is called the L^{th} order solution. See also chapter 3. In the next section we derive expressions

for the force $\underline{F}_i(\omega)$ and torque $\underline{T}_i(\omega)$ in terms of some coefficients, the last necessary step to determine the grand mobility matrix.

7.4 Force and torque as functions of the coefficients

The force $\underline{F}_i(\omega)$, exerted by the fluid on particle i, can be determined with the help of the following expression:

$$\underline{F}_i(\omega) = -\int_{S_i} \Pi(\underline{r},\omega)\cdot d\underline{S}_i \,, \tag{7.38}$$

with $\Pi(\underline{r},\omega)$ the pressure tensor and $d\underline{S}_i$ an infinitesimal element of surface pointing into the fluid. The pressure tensor has the following form:

$$\Pi(\underline{r},\omega) = p(\underline{r},\omega)I - 2\eta_o[\nabla \underline{v}(\underline{r},\omega)]^s \,, \tag{7.39}$$

where s stands for symmetric part. With this expression for the pressure tensor we can rewrite eq. (7.6) as

$$\nabla\cdot\Pi(\underline{r},\omega) = -\eta_o\alpha^2\underline{v}(\underline{r},\omega) \,. \tag{7.40}$$

In the case of our problem of two particles in an unbounded fluid, satisfying the linearized N.S. equations, it is convenient to split the expression for the pressure tensor into two parts, one defined with respect to the centre of particle 1 and the other with respect to the centre of particle 2. This means

$$\Pi(\underline{r},\omega) = \Pi_i(\underline{r}_i,\omega) + \Pi_j(\underline{r}_i+\underline{R}_{ij}) \quad \text{with: i=1, j=2 and vice versa} \,.$$

The tensor $\Pi_i(\underline{r}_i,\omega)$ is a function of the basic solutions $\underline{v}_{lm\sigma}(\underline{r}_i,\omega)$ and $p_{lm\sigma}(\underline{r}_i,\omega)$, with $\sigma\in\{\alpha,\beta,\gamma\}$. If we extend the basic solutions within the surfaces of both particles, then we see that $\Pi_i(\underline{r}_i,\omega)$ has only singularities within the surface S_i of particle i. Thus $\Pi_j(\underline{r}_i+\underline{R}_{ij})$ has no singularities within the surface S_i. Using Gauss' theorem and eq. (7.40) we can rewrite eq. (7.38) as

$$(7.41)\qquad \underline{F}_i(\omega) = -a^2\Big[(\Pi_i(\underline{r}_i,\omega)\cdot\hat{e}_r)d\Omega_i + \eta_o\alpha^2\Big[\underline{v}_j(\underline{r}_i+\underline{R}_{ij})d\underline{r}_i$$
$$|\underline{r}_i|\le a$$

$$= -a^2\Big[\Big[p_i(\underline{r}_i,\omega)\hat{e}_r d\Omega_i - \eta_o\Big[\frac{\partial}{\partial r_i}-\frac{1}{r_i}\Big]\Big]\underline{v}_i(\underline{r}_i,\omega)d\Omega_i$$

$$-\frac{\eta_o}{r_i}\Big[\nabla(\underline{r}_i\cdot\underline{v}_i(\underline{r}_i,\omega))d\Omega_i\Big]\Big|_{r_i\downarrow a} + \eta_o\alpha^2\Big[\underline{v}_j(\underline{r}_i+\underline{R}_{ij})d\underline{r}_i\,.$$
$$|\underline{r}_i|\le a$$

A complete evaluation of this expression would require excessive space. An outline of the calculation is to be found in appendix V. The final result is

$$(7.42)\qquad \underline{F}_i(\omega) = -\tfrac{1}{2}\eta_o\Big[n_{11}\Big[\alpha^i_{1,-1}(\omega)-\alpha^i_{1,1}(\omega)\Big]\hat{e}_x - in_{11}\Big[\alpha^i_{1,-1}(\omega)+\alpha^i_{1,1}(\omega)\Big]\hat{e}_y$$

$$+ 2n_{10}\alpha^i_{1,0}(\omega)\hat{e}_z\Big] + \tfrac{4}{3}\pi\eta_o a^3\alpha^2\underline{U}_i(\omega)\,.$$

In an analogous way we can determine the expression for the torque $\underline{T}_i(\omega)$, exerted by the fluid on particle i. The result is

$$(7.43)\quad \underline{T}_i(\omega) = -\frac{\eta_o a}{2g_1(\alpha a)}\Big[n_{11}\Big[\beta^i_{1,-1}(\omega)-\beta^i_{1,1}(\omega)\Big]\hat{e}_x - in_{11}\Big[\beta^i_{1,-1}(\omega)+\beta^i_{1,1}(\omega)\Big]\hat{e}_y$$

$$+ 2n_{10}\beta^i_{1,0}(\omega)\hat{e}_z\Big] + 8\pi\eta_o a^3\Big[\frac{\alpha a g_2(\alpha a)}{3g_1(\alpha a)}\Big]\underline{\Omega}_i(\omega)\,.$$

7.5 The derivation of the correlation matrix $\phi(\omega,\omega')$

The theory of Brownian motion is often based upon the Langevin equation. The Langevin equation for a Brownian particle in an unbounded fluid has, in the frequency representation, the following form [8]:

$$-i\omega m\underline{U}(\omega) = -\zeta(\omega)\cdot\underline{U}(\omega) + \underline{R}_f(\omega)\ , \tag{7.44}$$

where $\zeta(\omega) = -6\pi\eta_o aI(1+\alpha a+\frac{1}{9}\alpha^2a^2)$ and $\alpha = \sqrt{-i\omega\rho/\eta_o}$ with $\mathrm{Re}(\alpha)\geq 0$. The vector $\underline{R}_f(\omega)$ is the random force with: $<\underline{R}_f(\omega)> = 0$. The <..> stands for an ensemble average. Bedeaux and Mazur have derived the fluctuation dissipation (F.D.) theorem for this one particle case. Their result is [8]

$$<\underline{R}_f(\omega)\underline{R}_f^*(\omega')> = 4\pi k_B T\delta(\omega-\omega')\mathrm{Re}(\zeta(\omega))\ , \tag{7.45}$$

with k_B the Boltzmann constant and T the absolute temperature. With the help of the Langevin equation (7.44) and the F.D. theorem we are able to calculate the velocity autocorrelation function $\phi(\omega)$ of a Brownian particle. We study now the problem of two hydrodynamically interacting Brownian particles in an unbounded fluid. We are particularly interested in the effects of the hydrodynamic interaction on the velocity correlation functions, rotational velocity correlation functions and so on. All correlation functions can be summarized in the so called correlation matrix which we define as follows:

$$\boldsymbol{\phi}(\omega,\omega') = \begin{bmatrix} \boldsymbol{\phi}^{tt}(\omega,\omega') & \boldsymbol{\phi}^{tr}(\omega,\omega') \\ \boldsymbol{\phi}^{rt}(\omega,\omega') & \boldsymbol{\phi}^{rr}(\omega,\omega') \end{bmatrix} = \boldsymbol{\phi}^{\dagger}(\omega,\omega')\ , \tag{7.46}$$

with $\boldsymbol{\phi}^{tt}(\omega,\omega') = <\underline{U}(\omega)\underline{U}^*(\omega')>$, $\boldsymbol{\phi}^{rr}(\omega,\omega') = <\underline{\Omega}(\omega)\underline{\Omega}^*(\omega')>$,

$$\phi^{tr}(\omega,\omega') = <\underline{U}(\omega)\underline{\Omega}^*(\omega')> = \phi^{rt\dagger}(\omega,\omega') ,$$

where the dagger stands for Hermitean conjugation. In the following part of this section we shall give an outline of the determination of the correlation matrix $\phi(\omega,\omega')$ of a system of N particles of arbitrary form in an unbounded incompressible fluctuating fluid. The spontaneous fluctuations of the stress tensor causes the Brownian motion of the particles. For this system we use the theory of linear hydrodynamic fluctuations. The fluid velocity is described by the linearized stochastic Landau–Lifshitz equation of motion [2]:

$$(7.47) \qquad \eta_o \alpha^2 \underline{v}(\underline{r},\omega) = -\nabla\cdot\mathbf{P}(\underline{r},\omega) , \qquad \nabla\cdot\underline{v}(\underline{r},\omega) = 0 ,$$

with

$$\mathbf{P}(\underline{r},\omega) = \Pi(\underline{r},\omega) + \sigma(\underline{r},\omega) ,$$

where $\sigma(\underline{r},\omega)$ is the random stress tensor. The components of the stochastic stress tensor satisfy the following stochastic properties if averaged over an equilibrium ensemble:

$$(7.48) \qquad <\sigma(\underline{r},\omega)> = 0 ,$$

$$(7.49) \qquad <\sigma_{ij}(\underline{r},\omega)\sigma_{kl}(\underline{r}',\omega')> = 4\pi k_B T \eta_o (\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}-\tfrac{2}{3}\delta_{ij}\delta_{kl})\delta(\underline{r}-\underline{r}')\delta(\omega-\omega') .$$

The ensemble average of eq. (7.47) gives the N.S. equations.

We define the following column vectors to write the equations in a more compact form:

$$\underline{\kappa}(\omega) = \begin{bmatrix} \underline{F}(\omega) \\ \underline{T}(\omega) \end{bmatrix} , \quad \underline{\psi}(\omega) = \begin{bmatrix} \underline{U}(\omega) \\ \underline{\Omega}(\omega) \end{bmatrix} , \quad \underline{\chi}(\omega) = \begin{bmatrix} \underline{R}_f(\omega) \\ \underline{R}_t(\omega) \end{bmatrix} , \quad \text{with } \underline{F}(\omega) = \begin{bmatrix} \underline{F}_1(\omega) \\ \underline{F}_2(\omega) \\ \vdots \\ \underline{F}_N(\omega) \end{bmatrix} \text{ etc.}$$

$\underline{R}_t(\omega)$ is the random torque in the frequency representation with $<\underline{R}_t(\omega)> = 0$. The Langevin equation for the N particle problem is now

$$\underline{\kappa}(\omega) = -\zeta(\omega)\cdot\underline{\psi}(\omega) + \underline{\chi}(\omega)\ , \tag{7.50}$$

with $\zeta(\omega)$ the grand resistance matrix. Using the method of Bedeaux and Mazur one is able to derive the F.D. theorem for a system of N Brownian particles of arbitrary form in an unbounded fluid [8]:

$$<\underline{\chi}(\omega)\underline{\chi}^{*}(\omega')> = 4\pi k_B T\delta(\omega-\omega')\mathrm{Re}(\zeta(\omega))\ . \tag{7.51}$$

We can rewrite the correlation matrix $\phi(\omega,\omega')$ with the help of the compact notation introduced above:

$$\phi(\omega,\omega') = <\underline{\psi}(\omega)\underline{\psi}^{*}(\omega')>\ . \tag{7.52}$$

The vector $\underline{\psi}(\omega)$ can be determined with the Langevin equation (7.50). First we have to express the vector $\underline{\kappa}(\omega)$ as a function of $\underline{\psi}(\omega)$. We can do this as follows:

$$\underline{\kappa}(\omega) = \begin{bmatrix}\underline{F}(\omega)\\ \underline{T}(\omega)\end{bmatrix} = -i\omega\begin{bmatrix}\mathbf{M}\cdot\underline{U}(\omega)\\ \mathbf{N}\cdot\underline{\Omega}(\omega)\end{bmatrix} = -i\omega\mathbf{S}\cdot\underline{\psi}(\omega)\ , \tag{7.53}$$

with $\mathbf{M}$ the mass matrix and $\mathbf{N}$ the moment of inertia matrix. Both are diagonal. If the Brownian particles are spherical particles with the same radius and the same density the mass matrix is: $\mathbf{M} = m\mathbf{I}_{3N}$ with $\mathbf{I}_{3N}$ the 3N×3N identity matrix. In that case the inertia matrix becomes: $\mathbf{N} = \frac{2}{5}ma^2\mathbf{I}_{3N}$. We see that $\mathbf{S}$ is a real 6N×6N matrix. With this expression for $\underline{\kappa}(\omega)$ we can write for the Langevin equation (7.50)

$$-i\omega\mathbf{S}\cdot\underline{\psi}(\omega) = -\zeta(\omega)\cdot\underline{\psi}(\omega) + \underline{\chi}(\omega)\ . \tag{7.54}$$

Using the F.D. theorem (eq. (7.51)), we can now derive the following expression for the correlation matrix:

$$\phi(\omega,\omega') = 4\pi k_B T \delta(\omega-\omega') \mathrm{Re}((\zeta(\omega)-i\omega\mathbf{S})^{-1}) \equiv 2\pi\phi(\omega)\delta(\omega-\omega') \,. \tag{7.55}$$

The matrix **S** is known from eq. (7.53) and we are able to calculate the grand resistance matrix in the way described here. This means that we can study the effects of the hydrodynamic interactions on the correlation matrix and so are able to calculate the concentration dependence of the correlation matrix in dilute suspensions.

7.6 Two particle hydrodynamic interactions and the grand mobility matrix

In the first place we are interested in the components of the grand mobility matrix connected with a system of two particles in an unbounded fluid. To determine the ten independent components of the mobility matrix we need to express the coefficients $\alpha^i_{1m}(\omega)$ and $\beta^i_{1m}(\omega)$, for $m=-1,0,1$ and i=1,2 , in terms of the force $\underline{F}_i(\omega)$, the torque $\underline{T}_i(\omega)$, the velocity $\underline{U}_i(\omega)$ and the rotational velocity $\underline{\Omega}_i(\omega)$. With the help of the eqs. (7.42) and (7.43) we obtain

$$\alpha^i_{1,-1}(\omega)-\alpha^i_{1,1}(\omega) = -\frac{2}{\eta_o n_{11}} F_{ix}(\omega) + \frac{8\pi a^2 a^3}{3 n_{11}} U_{ix}(\omega) \,, \tag{7.56}$$

$$\alpha^i_{1,-1}(\omega)+\alpha^i_{1,1}(\omega) = -\frac{2i}{\eta_o n_{11}} F_{iy}(\omega) + \frac{8\pi a^2 a^3}{3 n_{11}} U_{iy}(\omega) \,, \tag{7.57}$$

$$\alpha^i_{1,0}(\omega) = -\frac{1}{\eta_o n_{10}} F_{iz}(\omega) + \frac{4\pi a^2 a^3}{3 n_{10}} U_{iz}(\omega) \,, \tag{7.58}$$

$$(7.59)\qquad \beta^{i}_{1,-1}(\omega)-\beta^{i}_{1,1}(\omega) = -\frac{2g_1(\alpha a)}{\eta_o a n_{11}} T_{ix}(\omega) + \frac{16\pi\alpha a^3}{3n_{11}} g_2(\alpha a)\Omega_{ix}(\omega)\,,$$

$$(7.60)\qquad \beta^{i}_{1,-1}(\omega)+\beta^{i}_{1,1}(\omega) = -\frac{2ig_1(\alpha a)}{\eta_o a n_{11}} T_{iy}(\omega) + i\frac{16\pi\alpha a^3}{3n_{11}} g_2(\alpha a)\Omega_{iy}(\omega)\,,$$

$$(7.61)\qquad \beta^{i}_{1,0}(\omega) = -\frac{g_1(\alpha a)}{\eta_o a n_{10}} T_{iz}(\omega) + \frac{8\pi\alpha a^3}{3n_{10}} g_2(\alpha a)\Omega_{iz}(\omega)\,.$$

The determination of the grand mobility matrix proceeds in the same way as described in chapter 3. We solve the set of linear equations (7.35)–(7.37) in such a way that we can express the coefficients $\alpha^{i}_{lm}(\omega)$ with $l\geq 2$, $\beta^{i}_{lm}(\omega)$ with $l\geq 2$, and $\gamma^{i}_{lm}(\omega)$ with $l\geq 1$ and i=1,2 in terms of the 12 coefficients $\alpha^{i}_{1m}(\omega)$ and $\beta^{i}_{1m}(\omega)$ with $m\in\{-1,0,1\}$ and i=1,2 which results in a set of 12 linear equations connecting the remaining coefficients with the boundary conditions (eqs. (7.27)–(7.29)). Substitution of the eqs. (7.56)–(7.61) for the coefficients $\alpha^{i}_{1m}(\omega)$ and $\beta^{i}_{1m}(\omega)$ into the remaining set of linear equations and some rearrangements gives the final result

$$(7.62)\qquad \begin{bmatrix}\underline{U}(\omega)\\ \underline{\Omega}(\omega)\end{bmatrix} = -\begin{bmatrix}\boldsymbol{\mu}^{tt}(\omega) & \boldsymbol{\mu}^{tr}(\omega)\\ \boldsymbol{\mu}^{rt}(\omega) & \boldsymbol{\mu}^{rr}(\omega)\end{bmatrix}\cdot\begin{bmatrix}\underline{F}(\omega)\\ \underline{T}(\omega)\end{bmatrix} \quad \text{with } \underline{U}(\omega) = \begin{bmatrix}\underline{U}_1(\omega)\\ \underline{U}_2(\omega)\end{bmatrix} \text{ etc.}$$

In fig.2 we show the 10 independent components of the grand mobility matrix as a function of the dimensionless parameter $|\alpha a|$ for some values of $x = \frac{a}{R}$. The results are based on calculations where we used an upper limit L=10 for the indices l and p (see section 3). To understand these figures it is important to derive a relation between the dimensionless parameter $|\alpha a|$ and the dimensionless time $\tau_B = (6\pi\eta_o a/m)t$ with m the mass of the spherical particle and t the ordinary time. We have: $|\alpha a| = a\sqrt{\omega\rho/\eta_o} \equiv \sqrt{\omega_0}$. We can relate ω_0 with a dimensionless time τ_0:

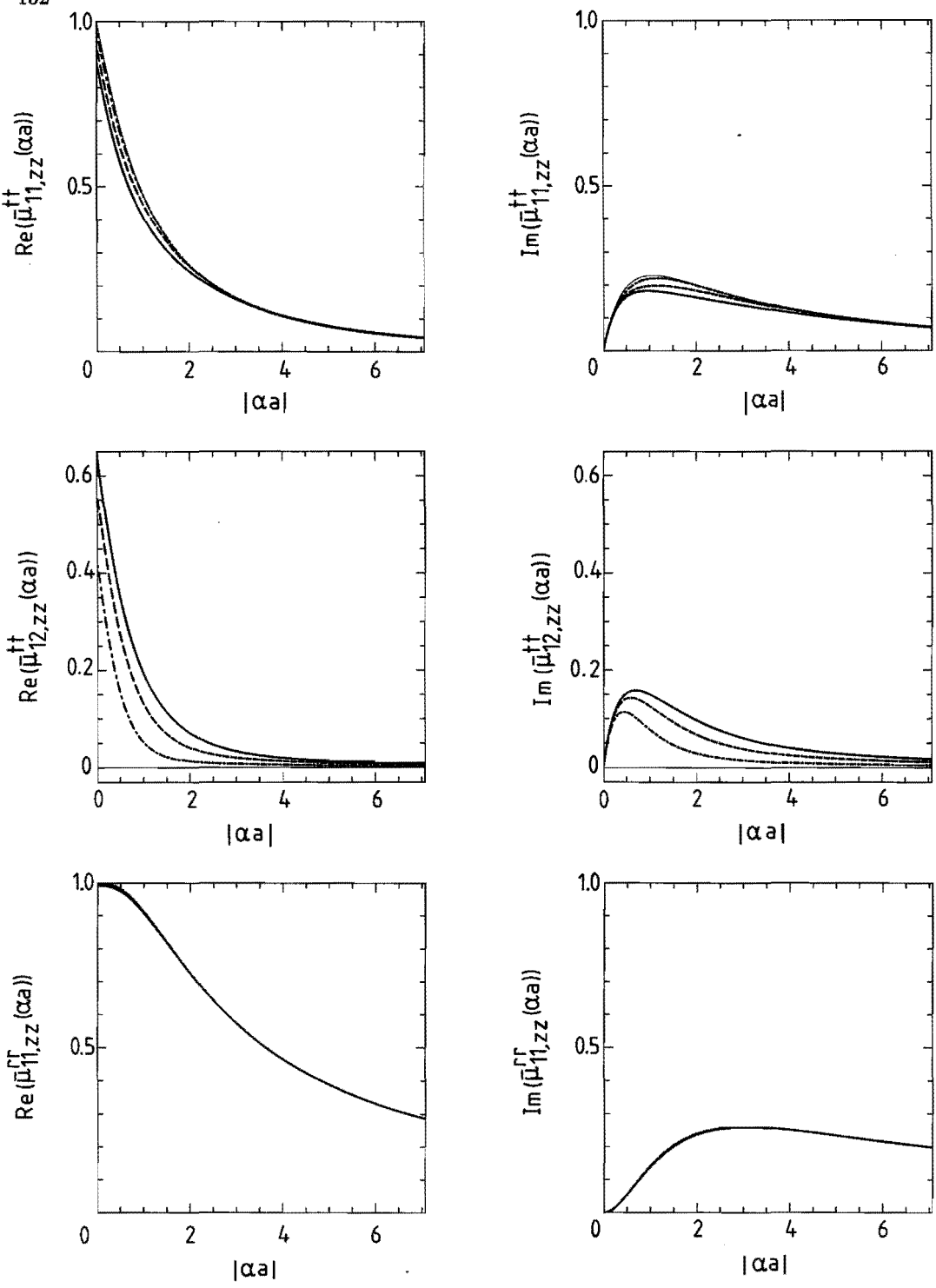

Fig.2. *The real and imaginary parts of the normalized components of the grand mobility matrix plotted versus $|\alpha a|$ for several values of $x=\frac{a}{R}$, with: $\bar{\mu}^{tt} = 6\pi\eta_o a\mu^{tt}$, $\bar{\mu}^{tr} = 8\pi\eta_o a^2\mu^{tr}$ and $\bar{\mu}^{rr} = 8\pi\eta_o a^3\mu^{rr}$. Bold solid curve: $x=0.45$; dashed curve: $x=0.4$; dash–dotted curve: $x=0.3$; thin solid curve: $x=0$.*

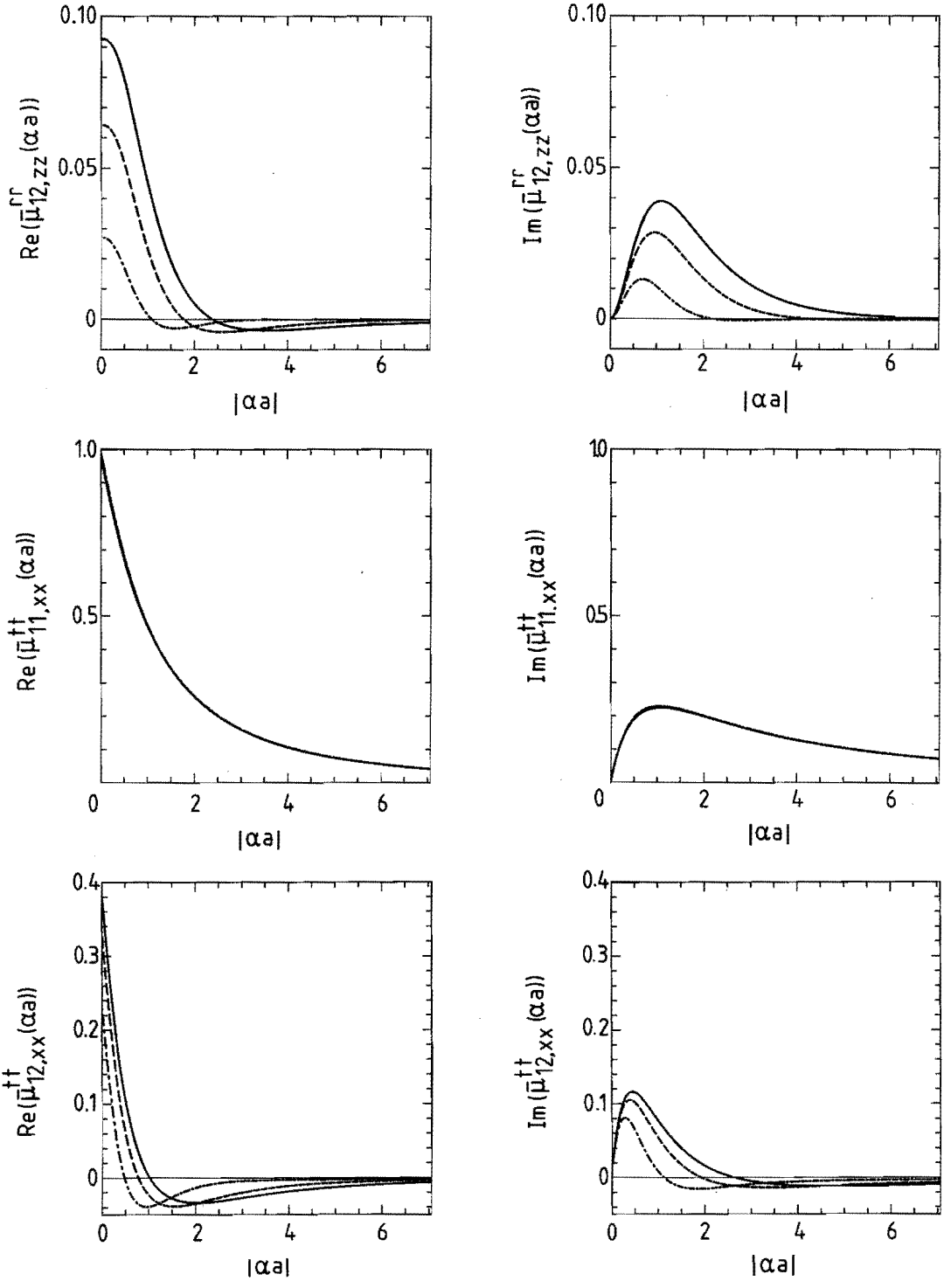
0.10
0.05
0
Re($\bar{\mu}^{rr}_{12,zz}$(αa))
Im($\bar{\mu}^{rr}_{12,zz}$(αa))
1.0
0.5
Re($\bar{\mu}^{tt}_{11,xx}$(αa))
10
0.5
Im($\bar{\mu}^{tt}_{11,xx}$(αa))
0.4
0.3
0.2
0.1
0
Re($\bar{\mu}^{tt}_{12,xx}$(αa))
Im($\bar{\mu}^{tt}_{12,xx}$(αa))
0
2
4
6
|αa|

Fig.2. (cont.).

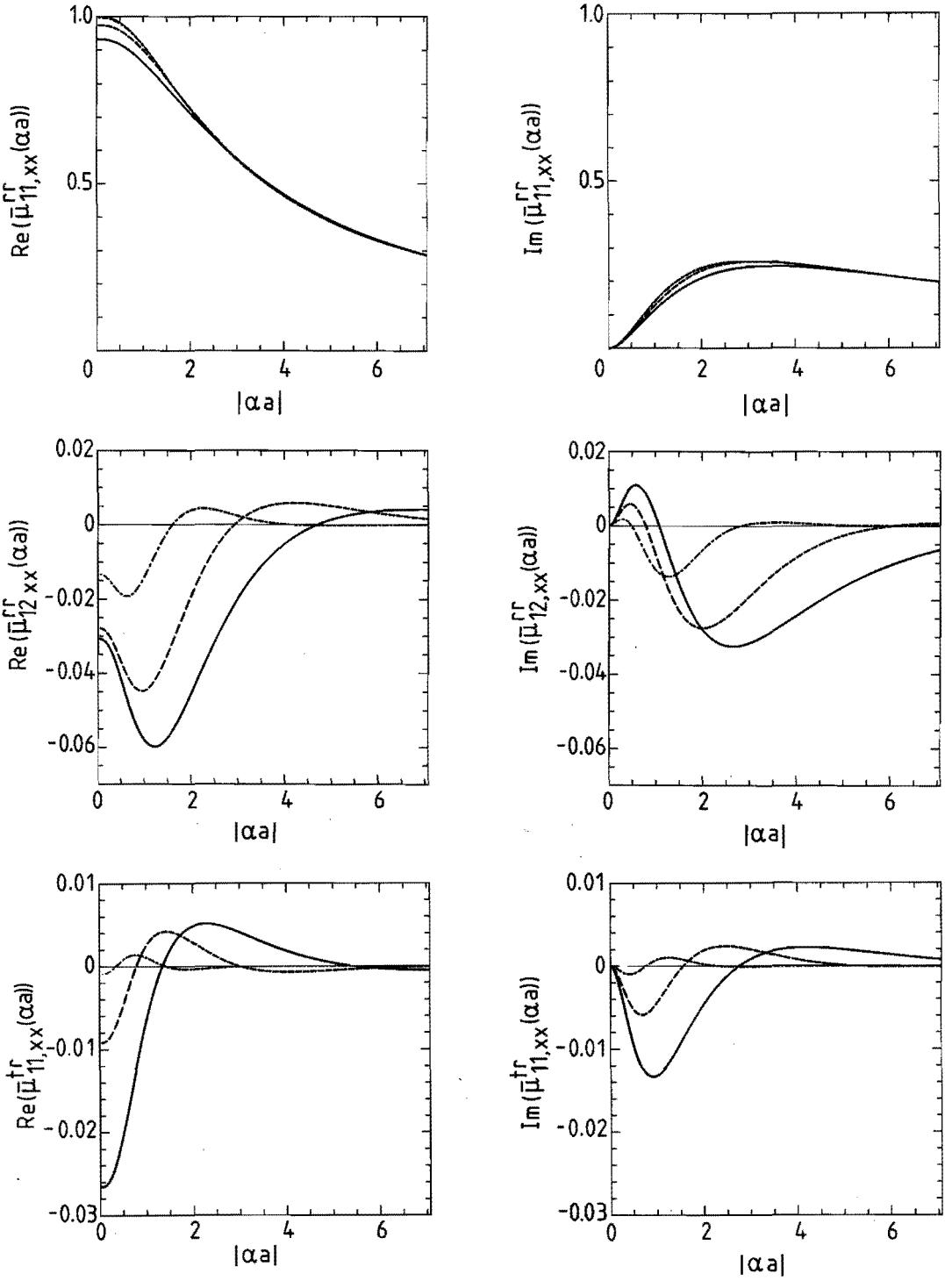
Re($\bar{\mu}^{rr}_{11,xx}(\alpha a)$)
Im($\bar{\mu}^{rr}_{11,xx}(\alpha a)$)
Re($\bar{\mu}^{rr}_{12,xx}(\alpha a)$)
Im($\bar{\mu}^{rr}_{12,xx}(\alpha a)$)
Re($\bar{\mu}^{tr}_{11,xx}(\alpha a)$)
Im($\bar{\mu}^{tr}_{11,xx}(\alpha a)$)
|αa|
1.0
0.5
0.02
0
-0.02
-0.04
-0.06
0.01
-0.01
-0.03
0
2
4
6

Fig.2. (cont.).

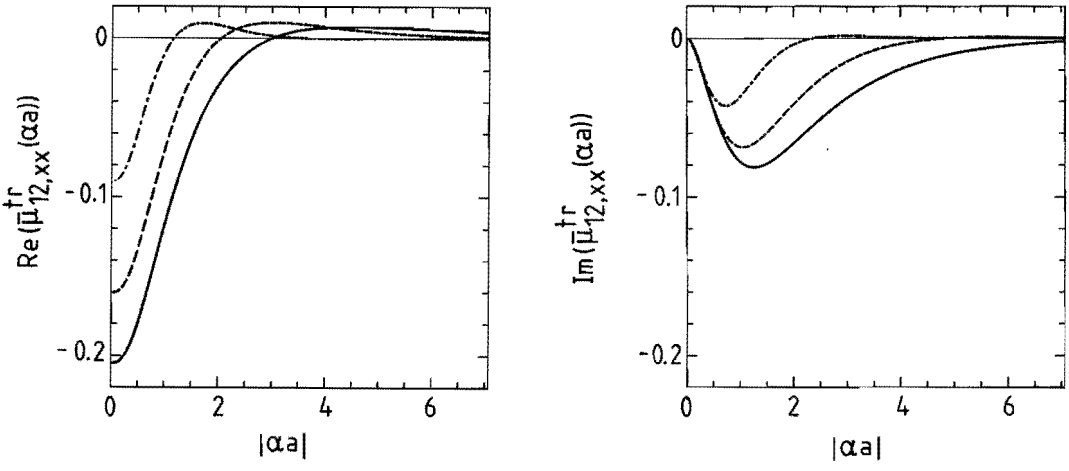

Fig.2. (cont.).

$$\omega_0 \longleftrightarrow \frac{1}{\tau_0}\,, \quad \text{where } \tau_0 = \frac{\eta_o}{\rho a^2}\,t\,.$$

The relation between the dimensionless times τ_B and τ_0 is:

$$\tau_B = \frac{9}{2\sigma}\,\tau_0\,, \tag{7.63}$$

where $\sigma = \frac{\rho_s}{\rho}$, the ratio between the density of the particle and the fluid density. The value of $|\alpha a|$ which is related with $\tau_B = 1$ is: $|\alpha a| = \sqrt{(9/2\sigma)} = O(1)$ if $\sigma \simeq 1$. We have no knowledge of earlier results to compare ours with. There is some theory developed by van Saarloos and Mazur [9] and Pienkowska [10]. Van Saarloos and Mazur derived expressions for some components of the grand mobility matrix and studied expansions of their

expressions into powers of αa and a/R. The disadvantage of these power expansions is the limited range of validity. Pienkowska studied friction and mobility relations in the long time limit, which means that this paper concerns the hydrodynamic interactions close to the steady state conditions. The disadvantage of the results of Pienkowska is the limited range of validity, too.

7.7 Time dependent diffusion coefficients

We are able to calculate the grand mobility matrix and then the correlation matrix as derived in section 5. We have studied the behaviour of this correlation matrix in the case of dilute suspensions where the volume fraction $\varphi = \frac{4}{3}\pi a^3 n_o << 1$. We have to take into account only the two particle hydrodynamic interactions. Using the simplest form of the pair distribution function,

$$(7.64) \qquad g(\underline{R}) = \begin{cases} 0\ , & |\underline{R}| < 2a\ , \\ 1\ , & |\underline{R}| \geq 2a\ , \end{cases}$$

we can write for the correlation matrix:

$$(7.65) \quad <\phi(\omega,\omega')>_c = 4\pi k_B T \delta(\omega-\omega') \mathrm{Re}(<(\zeta(\omega)-i\omega\mathbf{S})^{-1}>_c) = \phi_0(\omega,\omega') + \varphi\phi_1(\omega,\omega')\ ,$$

where $<..>_c$ denotes an average over all configurations of the N particles. $\phi_0(\omega,\omega')$ is the correlation matrix for an infinitely diluted suspension and $\varphi\phi_1(\omega,\omega')$ is the correction due to the two particle hydrodynamic interactions. In eq. (7.65) the correlation matrix is a function of frequency. For many applications we are more interested in the Fourier transform of eq. (7.65). The Fourier transform of $\phi(\omega,\omega')$ is

$$(7.66)\qquad \phi(t,t+\tau) = \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-i\omega t}e^{i\omega'(t+\tau)}\phi(\omega,\omega')d\omega d\omega'$$

$$= \frac{k_B T}{\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-i\omega t}e^{i\omega'(t+\tau)}\delta(\omega-\omega')\mathrm{Re}((\zeta(\omega)-i\omega S)^{-1})d\omega d\omega'$$

$$= \frac{k_B T}{\pi}\int_{-\infty}^{+\infty} e^{i\omega\tau}\mathrm{Re}((\zeta(\omega)-i\omega S)^{-1})d\omega = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega\tau}\phi(\omega)d\omega = \phi(\tau)\,.$$

In the last step we used the fact that $\mathrm{Re}((\zeta(\omega)-i\omega S)^{-1}) = \mathrm{Re}((\zeta(-\omega)+i\omega S)^{-1})$, which follows from the reality condition $\mu(-\omega) = \mu(\omega)^*$. The Fourier transformation is a linear operation and for that reason we can write

$$(7.67)\qquad <\phi(\tau)>_c = \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-i\omega t}e^{i\omega'(t+\tau)}<\phi(\omega,\omega')>_c d\omega d\omega'$$

$$= \frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-i\omega t}e^{i\omega'(t+\tau)}(\phi_0(\omega,\omega') + \varphi\phi_1(\omega,\omega'))d\omega d\omega' = \phi_0(\tau) + \varphi\phi_1(\tau)\,.$$

We are especially interested in some components of the correlation matrix such as

$$(7.68)\qquad <\phi_{ij}^{tt}(\tau)>_c = <<\underline{U}_i(t)\underline{U}_j(t+\tau)>>_c \equiv \phi_{ij}(\tau)I_3\,.$$

It is possible to plot $\phi_{ij}(\tau)$ as a function of time τ for several values of σ, the ratio of the density of the particles and the fluid density. Then we are able to compare the velocity correlation functions for different values of the volume fraction φ. There is one drawback in following this procedure: the velocity correlation functions fall off to small values very

quickly. Instead of studying the behaviour of $\phi(\tau)$ we can study the behaviour of $D(\tau)$, the time dependent diffusion matrix. We define this matrix as

$$(7.69) \qquad D(\tau) \equiv \int_0^\tau \phi(\tau')d\tau' \, .$$

This integral is a linear operation and we can determine the configuration average of the time dependent diffusion matrix in a relatively simple way by using the configuration average of the correlation matrix:

$$(7.70) \qquad <D(\tau)>_c = \int_0^\tau <\phi(\tau')>_c d\tau' = \int_0^\tau \phi_0(\tau')d\tau' + \varphi\int_0^\tau \phi_1(\tau')d\tau'$$

$$= D_0(\tau) + \varphi D_1(\tau) \, .$$

We are only interested in some components of the diffusion matrix such as

$$(7.71) \qquad <D_{ij}^{tt}(\tau)>_c = \int_0^\tau \phi_{ij}(\tau')d\tau' I_3 \equiv D_{ij}(\tau)I_3 \, .$$

In fig.3 we have plotted $D_{11}(\tau)$ for several values of σ and φ as a function of the dimensionless time τ_B. The time scales used in these figures are compatible with the assumption that the configuration of the particles remains nearly constant (see short discussion below eq. (7.8)). Under this condition we should formally speak of the short time diffusion coefficient $D_{11}(\tau)$. The compatibility can be shown by a comparison of diffusion displacement and particle radius. We write

$$(7.72) \qquad 6D_o t = <|\Delta \underline{r}(t)|^2> \approx \epsilon^2 a^2 \, ,$$

and obtain

$$\tau_B \approx \frac{9\pi}{2} \frac{a\rho\nu^2}{k_B T\sigma} \epsilon^2 . \tag{7.73}$$

Suppose $\epsilon \approx 0.01$, then, in the case of particles with radius of 0.1μm dispersed in water at room temperature, we obtain $\tau_B \approx 10^3 - 10^5$ depending, of course, on the value of σ. We compare the behaviour of the correlation functions for the following values of the volume fraction: $\varphi = 0$, 0.1, 0.2 and 0.3. Although we seem to go beyond the range of validity of this theory by excluding more particle hydrodynamic interactions we expect that a discussion on the behaviour of the correlation functions in the proposed range of φ will make sense because we know that, in the Stokes limit, $D_s^t \simeq D_o(1-1.83\varphi)$ is a reasonable approximation if $\varphi \lesssim 0.3$ (see also eq. (5.37)). This linear behaviour of D_s^t as a function of φ is confirmed by several authors with experimental evidence [11, 12]. We also refer to a short discussion about this remarkable point in a paper of van Veluwen et al. [13]. This behaviour is confirmed by Stokesian dynamics simulation results of Phillips et al. too [14]. With this evidence we do not conclude that up to $\varphi \simeq 0.3$ one can study transport coefficients by including two particle hydrodynamic interactions only. There are many examples where this is not the case, e.g. the sedimentation problem. The conclusion is that in the case of the translational self–diffusion coefficient D_s^t the effects of three and more particle interactions seem small if $\varphi \lesssim 0.3$ and the two particle hydrodynamic interactions are thus dominant. At this point there is no reason to expect that $D_{11}(\tau)$, as a function of φ, will behave very differently for $\varphi \lesssim 0.3$, so we can discuss the results for $D_{11}(\tau)$ in a qualitative way keeping in mind that we expect that three and more particle interactions have small influence on $D_{11}(\tau)$. However, we do expect that the three and more particle hydrodynamic interactions become important enough to influence $D_{11}(\tau)$ at higher values of φ so we do not discuss these correlation functions for $\varphi > 0.3$, except noting that, even for higher volume fractions, the order φ correction to $D_{11}(\tau)$ remains important. From these figures (fig. 3) we learn something about the velocity autocorrelation function $\phi_{11}(\tau)$

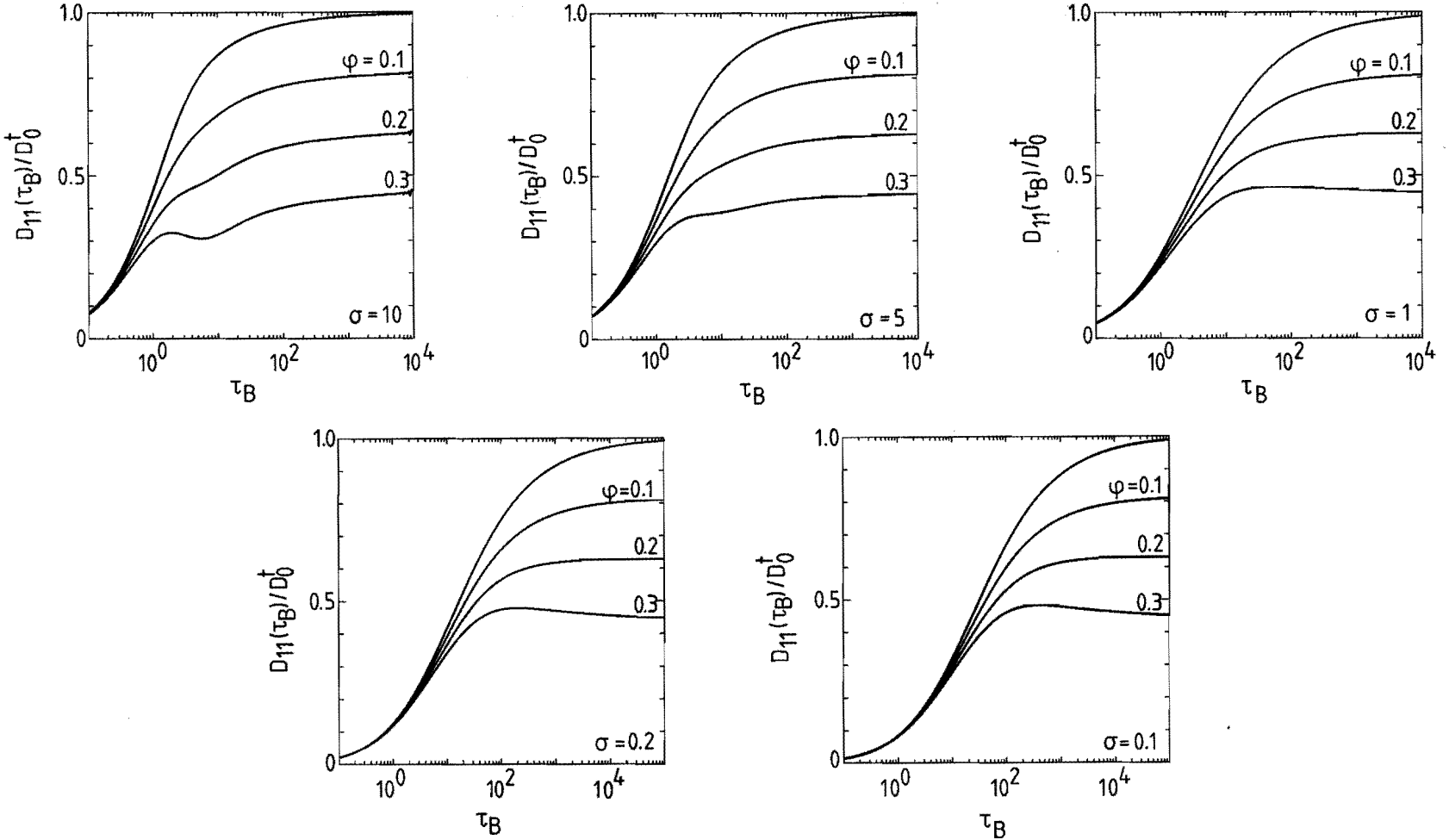

Fig.3. *The normalized time dependent diffusion coefficient, $D_{11}(\tau_B)/D_o^t$, plotted for several values of the volume fraction φ versus the dimensionless time τ_B. The ripples in the curves for $\sigma=10$ are a consequence of the numerical Fourier transformation.*

because we have (see eq. (7.71))

$$\frac{dD_{11}(\tau)}{d\tau} = \phi_{11}(\tau)\,, \tag{7.74}$$

thus the sign of $\phi_{11}(\tau)$ determines the slope of $D_{11}(\tau)$. Looking at fig. 3 we can see that in the case φ=0.1 and φ=0.2 the velocity autocorrelation function $\phi_{11}(\tau)$ is a decreasing function of τ except in the case σ=10 because then we see two inclination points, so $\phi_{11}(\tau)$ has then a positive local minimum and a local maximum. The case φ=0.3 is more difficult. In the case σ=10 we can conclude that the velocity autocorrelation function $\phi_{11}(\tau)$ has a minimum, which is negative, and a local maximum, which is positive. After the local maximum the correlation function goes to zero. In the case σ=5 we see that $D_{11}(\tau)$ has two inclination points, so $\phi_{11}(\tau)$ has a positive local minimum and a local maximum. After the last local maximum the correlation function decreases to zero. For the smaller values of σ we see that $D_{11}(\tau)$ has a maximum and, as a consequence, we can conclude that $\phi_{11}(\tau)$ becomes negative and goes to zero after reaching a minimum. These minima occur at large times compared to the Brownian time, corresponding to τ_B=1. Finally we study the long time limit $\tau\to\infty$ of the diffusion coefficients $D_{11}(\tau)$ and $D_{12}(\tau)$. This long time limit should be read in the context of the assumptions made earlier (see eq. (7.8)) which means that we study the limit that $\tau_B >> 1$ but τ_B still small enough in comparison to the time needed for changes of particle configuration. We know (eq. (7.66)) that

$$\phi^{tt}_{ij}(\tau) = \frac{k_B T}{\pi} \int_{-\infty}^{+\infty} e^{-i\omega\tau} [\mathrm{Re}((\zeta(\omega) - i\omega S)^{-1})]^{tt}_{ij} d\omega\,. \tag{7.75}$$

The term in square brackets is an even function of frequency and real. For that reason $\phi^{tt}_{ij}(\tau)$ is an even function of τ and we can write

$$(7.76)\qquad \int_{-\infty}^{+\infty} e^{i\omega\tau}\phi_{ij}^{tt}(\tau)d\tau = 2\int_{0}^{\infty}\phi_{ij}^{tt}(\tau)\cos(\omega\tau)d\tau = 2k_BT[\mathrm{Re}((\zeta(\omega)-i\omega S)^{-1})]_{ij}^{tt}\,.$$

Using the relation derived above and eq. (7.71) we obtain the following expression:

$$(7.77)\qquad \lim_{\tau\to\infty}\langle D_{ij}(\tau)\rangle_c = \int_{0}^{\infty}\langle\phi_{ij}^{tt}(\tau')\rangle_c d\tau' =$$

$$k_BT\lim_{\omega\to 0}\langle[\mathrm{Re}((\zeta(\omega)-i\omega S)^{-1})]_{ij}^{tt}\rangle_c \equiv k_BT\lim_{\omega\to 0}\langle\Psi_{ij}^{tt}(\omega)\rangle_c\,.$$

The calculation of the configurational average before taking the limit $\omega\to 0$ is essential because in that order the screening effect, caused by the retardation of the hydrodynamic interactions (resulting in an order $(a/R)^3$ instead of an order a/R contribution to the interactions among particles in a dilute suspension [9]), is retained and the configurational integral converges. The calculation of $\langle\Psi_{11}^{tt}(\omega)\rangle_c$ proceeds in the same way as presented in chapter 3 and the result for the long time limit of $D_{11}(\tau)$ is

$$(7.78)\qquad \lim_{\tau\to\infty} D_{11}(\tau) = D_o(1-1.83\varphi)\,,$$

where D_o is the Stokes–Einstein diffusion coefficient. This result is equivalent to the first order virial expansion of the short time self–diffusion coefficient already calculated by Batchelor [15]. In the Stokes limit D_{12} cannot be determined directly but in contrast $\langle\Psi_{12}^{tt}(\omega)\rangle_c$ can be calculated if we write

$$(7.79)\qquad \langle\Psi_{12}^{tt}(\omega)\rangle_c = \langle\nu_1(\omega)\rangle_c + \langle\nu_2(\omega)\rangle_c\,.$$

In this equation $\nu_1(\omega)$ represents that part of $\Psi_{12}^{tt}(\omega)$ which gives in the Stokes limit ($\omega\to 0$)

the so called Oseen part and dipolar part of the mobility tensor μ_{12}^{tt}. The tensor $\nu_2(\omega)$ contains in the Stokes limit the remaining part of the mobility tensor μ_{12}^{tt}. We determine can $<\nu_1(\omega)>_c$ analytically. We write

$$(7.80)\qquad \nu_1(\omega) = -\mathrm{Re}\left[2A(\alpha a)\frac{k_1(\alpha R)}{\alpha R} - 2B(\alpha a)x^3\right]\hat{R}\hat{R} + \mathrm{Re}\left[A(\alpha a)(k_0(\alpha R) + \frac{k_1(\alpha R)}{\alpha R}) - B(\alpha a)x^3\right](I-\hat{R}\hat{R}),$$

with

$$(7.81)\qquad A(\alpha a) = \frac{1}{6\pi\eta_o a}\frac{27\pi}{4\alpha^5 a^5 k_2^2(\alpha a)}\left[\frac{1+\alpha a+\frac{1}{3}\alpha^2 a^2}{1+\alpha a+\frac{1}{9}(2\sigma+1)\alpha^2 a^2}\right]^2,$$

$$(7.82)\qquad B(\alpha a) = \frac{1}{6\pi\eta_o a}\frac{3}{2\alpha^2 a^2}\left[\frac{1+\alpha a+\frac{1}{3}\alpha^2 a^2}{1+\alpha a+\frac{1}{9}(2\sigma+1)\alpha^2 a^2}\right]^2.$$

Both terms containing the modified spherical Bessel functions can be configurationally averaged without problems. Using the simplest form of the pair distribution function $g(\underline{R})$ (eq. (7.64)) we obtain

$$(7.83)\qquad \int_{2a}^{\infty} k_0(\alpha R)R^2 dR = 4a^3\frac{k_1(2\alpha a)}{\alpha a},$$

$$(7.84)\qquad \int_{2a}^{\infty}\frac{k_1(\alpha R)}{\alpha R}R^2 dR = 2a^3\frac{k_0(2\alpha a)}{\alpha^2 a^2} - \frac{\pi}{2\alpha^3}\mathrm{Ei}(-2\alpha a),$$

with Ei(z) the exponential integral [6]. We now obtain for $<\nu_1(\omega)>_c$

$$(7.85)\qquad <\nu_1(\omega)>_c = \mathrm{Re}\left[8\varphi I A(\alpha a)\frac{k_1(2\alpha a)}{\alpha a} - B(\alpha a)n_o a^3\right]\int g(\underline{R})\frac{(I-3\hat{R}\hat{R})}{R^3}\,d\underline{R}.$$

The second term in eq. (7.85) is a conditionally convergent integral. This integral has been solved in the literature [16]. The final result for $<\nu_1(\omega)>_c$ is

$$(7.86) \qquad <\nu_1(\omega)>_c = \varphi \mathrm{IRe}\left[8A(\alpha a)\frac{k_1(2\alpha a)}{\alpha a} - 2B(\alpha a)\right] .$$

It is not difficult to obtain the limit $\omega \to 0$ (or $\alpha \to 0$):

$$(7.87) \qquad \lim_{\omega \to 0} 6\pi\eta_o a<\nu_1(\omega)>_c = -5\varphi \mathrm{I} .$$

We have calculated $<\nu_2(\omega)>_c$ numerically. After taking the limit $\omega \to 0$ we obtain

$$(7.88) \qquad \lim_{\omega \to 0} 6\pi\eta_o a<\nu_2(\omega)>_c = 0.28\varphi \mathrm{I} .$$

The final result is

$$(7.89) \qquad \lim_{\tau \to \infty} D_{12}(\tau) = -4.72\varphi D_o .$$

Combination of eqs. (7.78) and (7.89) results in the virial expansion for the sedimentation velocity

$$(7.90) \qquad \frac{U_o}{D_o} \lim_{\tau \to \infty} (D_{11}(\tau)+D_{12}(\tau)) = (1-6.55\varphi)U_o ,$$

with U_o the sedimentation velocity of a Brownian particle in an infinitely diluted suspension.

7.8 Conclusion

In this chapter we have derived the set of linear equations necessary to calculate the components of the grand mobility matrix of a two particle system with retarded hydrodynamic interactions. With the components of the mobility matrix we are able to study the correlation functions of the Brownian particles. From these correlation functions we can draw some conclusions. The presented results of the time dependent self–diffusion coefficient $D_{11}(\tau)$ gives evidence for small oscillatory behaviour of the velocity autocorrelation function of the Brownian particles. The oscillatory behaviour of the velocity autocorrelation function is a subtle effect caused by so called backscattering effects via the fluid molecules. In a hard sphere fluid, backscattering is the effect that the velocity of a tagged particle is, on the average, reversed by collisions between near neighbours. In the case of suspensions there are two sources contributing to the backscattering effect. First we have backscattering via the fluid molecules, which produce the backflow pattern. In the case of a Brownian particle in an infinitely diluted suspension this backflow pattern gives rise to the memory effects and long time tails [3,17]. Another contribution is direct backscattering via direct collisions of the suspended particles. This point has not been studied in this chapter. For a further discussion of backscattering effects and related topics see e.g. ref. [18]. It should be pointed out that, despite the oscillations, the velocity autocorrelation function is not always negative. Formally the name backscattering is connected with the negative part of the correlation function, but we use the term in a more general sense. In the case under consideration it is easy to imagine that the oscillations are caused by fluid backflow, induced by e.g. the time dependent motion of the first particle and returning to that particle after interaction with the second particle. The second particle is necessary for the oscillatory behaviour because in the one particle problem the velocity autocorrelation function does not show this behaviour. It can be compared with the behaviour of correlation functions of a tagged particle in a hard sphere fluid. Obviously

there are great differences between a hard sphere fluid and a suspension of hard spheres but nevertheless the correlation functions behave in a similar way. See in this context the simulation results of Lennard–Jones fluids (e.g. ref. [19]). It is important to note that also differences exist, the oscillations shown in fig. 3 are much smaller and take place on larger time scales. A further step would be the extension of the presented method by inclusion of three and more particle clusters, so that possible enhancement of the effects of retarded hydrodynamic interactions on the correlation functions could be investigated.

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Chapter 8 CONCLUSIONS

8.1 Quasistatic hydrodynamic interactions

In this thesis a method has been described to study hydrodynamic interactions among spherical particles. In the quasistatic case we succeeded in reformulating the problem of N hydrodynamically interacting spherical particles in terms of a set of linear algebraic equations. The advantage of this formulation is that it can easily be solved to obtain results for the components of the mobility matrix. The numerical implementation is simple. It shows that the results converge faster and more systematically than the results obtained by using the reflection method (chapter 3). In line with the ideas of Saito, we have studied the high frequency effective viscosity, which can easily be evaluated with the presented method. The final result is encouraging as a comparison with experimental and simulation data indicates that three and more particle hydrodynamic interactions give only subtle corrections to our expression (eq. (4.35)). In order to confirm this conclusion it is necessary to study the higher order contributions.

The advantages of our method are particularly clear if we consider three particle hydrodynamic interactions. The study of some special three particle configurations has given us some insight in the convergence behaviour of some components of the mobility matrix. With the described method it is not difficult to obtain these components for an arbitrary configuration of the three particles, even at small interparticle spacings with an exception of touching spheres. With these results we have been able to determine the virial expansions, up to φ^2, of the translational and rotational self–diffusion coefficient, which are in agreement with experimental results and simulation data up to $\varphi \approx 0.4$ (eqs. (5.37) and (5.38)). The second order virial coefficient of D_s^t is lower than expected from the literature.

The difference from some of these literature values can be explained: only one term of the reflection expansion is used (Beenakker) or fitting procedures seem unreliable. The virial expansion of D_s^r is in good agreement with experimental and simulation data up to higher volume fractions. We have also presented virial expansions for translational and rotational sedimentation velocities, eqs. (5.46) and (5.51). Our expression for the sedimentation velocity cannot be used up to large values of φ, however the expression derived by our method is an improvement in comparison with the Batchelor expression (eq. (1.1)). Furthermore we can conclude that the second order virial coefficient is much higher than recent estimates of fitting procedures. From our results it is obvious that virial expansions based on fitting procedures should not be trusted, explicit calculations are indispensable. The virial expansion of the rotational sedimentation velocity agrees very well with simulation data.

8.2 Retarded hydrodynamic interactions

The method presented to study the quasistatic hydrodynamic interactions has been extended to the problem of retarded hydrodynamic interactions among spherical particles. Apart from the satisfactory convergence behaviour, there is another important advantage, the fact namely that we have been able to obtain expressions for the components of the grand mobility matrix for the whole frequency domain. Some components of the grand mobility matrix can be used to determine the Fourier transforms of correlation functions of Brownian particles. With the inverse Fourier transforms of these expressions we are able to determine the time correlation functions including hydrodynamic pair interactions. These expressions can be configurationally averaged without problems because screening effects remove divergency problems, although in some cases conditionally convergent integrals must be taken into consideration. We have studied the time dependent diffusion coefficient

and shown the oscillatory behaviour of the velocity autocorrelation function for higher volume fractions in some cases (see chapter 7). For a correct description of this phenomenon the inclusion of three and more particle retarded hydrodynamic interactions is necessary. This extension is in principle possible in a similar way as in the quasistatic case.

8.3 Final remarks

Finally we want to point out that many more problems might be worked out with our method. First of all higher order hydrodynamic interactions could be studied on fast computers for both the quasistatic and the retarded hydrodynamic interactions between spherical particles. The method to determine the effective viscosity of hard sphere suspensions can be extended to include three particle hydrodynamic interactions. With the results of chapter 4 the conclusions could be decided to be correct. Besides these straightforward extensions a study of the problem of a one, two or three dimensional lattice of colloidal particles can be taken up, as the presented formulation seems suitable for that purpose. In the past some attention was paid to this kind of problems [1,2]. Furthermore the problem of hydrodynamically interacting ellipsoids can be studied by using an expansion in ellipsoidal harmonics (see an article by Kim [3]). It is not clear if these ideas can be worked out but a preliminary study might be worthwile.

References

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Appendix I

The calculation of the inner product relations in the eqs. (2.36)–(2.38) is performed with the help of integrals given below. We shall not prove these relations. First define the following short hand notations:

$$F^{pq}_{ij} = \tfrac{1}{2}\delta_{l,p}\Big[n_{11}\sqrt{(p-q)(p+q+1)}\; Y_{1,1}(\xi_{ij},\eta_{ij})\delta_{m,q+1} - \tfrac{1}{2}n_{11}\sqrt{(p+q)(p-q+1)} \times Y_{1,-1}(\xi_{ij},\eta_{ij})\delta_{m,q-1} - 2n_{10}qY_{1,0}(\xi_{ij},\eta_{ij})\delta_{m,q}\Big] ,$$

$$G^{pq}_{ij} = \tfrac{1}{2}\delta_{l,p+1}\Big[n_{11}\sqrt{(p+q+1)(p+q+2)}\; Y_{1,1}(\xi_{ij},\eta_{ij})\delta_{m,q+1} + n_{11}\sqrt{(p-q+1)(p-q+2)} \times Y_{1,-1}(\xi_{ij},\eta_{ij})\delta_{m,q-1} + 2n_{10}\sqrt{(p+q+1)(p-q+1)}\; Y_{1,0}(\xi_{ij},\eta_{ij})\delta_{m,q}\Big] ,$$

$$H^{pq}_{ij} = \tfrac{1}{2}\delta_{l,p-1}\Big[n_{11}\sqrt{(p-q)(p-q-1)}\; Y_{1,1}(\xi_{ij},\eta_{ij})\delta_{m,q+1} + n_{11}\sqrt{(p+q)(p+q-1)} \times Y_{1,-1}(\xi_{ij},\eta_{ij})\delta_{m,q-1} - 2n_{10}\sqrt{(p+q)(p-q)}\; Y_{1,0}(\xi_{ij},\eta_{ij})\delta_{m,q}\Big] ,$$

$$\Gamma^{ji}_{lm;pq} = \frac{n_{pq}}{(p+q)!}\, M^{ji}_{lm;pq}(\underline{R}_{ij}) .$$

The integrals are:

$$\int (\underline{R}_{ij}\times\underline{A}_{lm}(\theta,\varphi))\cdot\underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = i(2p+1)R_{ij}F^{pq}_{ij} ,$$

$$\int (\underline{R}_{ij}\times\underline{A}_{lm}(\theta,\varphi))\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = 0 ,$$

$$\int (\underline{R}_{ij}\times\underline{A}_{lm}(\theta,\varphi))\cdot\underline{C}^{*}_{pq}(\theta,\varphi)d\Omega = -p\left[\frac{2p+3}{2p+1}\right]^{1/2}R_{ij}G^{pq}_{ij} ,$$

$$\int \underline{\underline{R}}_{ij} Y_{lm}(\theta,\varphi)\cdot \underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = -\left[\frac{2p+1}{2p-1}\right]^{1/2} R_{ij} H^{pq}_{ij} ,$$

$$\int \underline{\underline{R}}_{ij} Y_{lm}(\theta,\varphi)\cdot \underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = -\left[\frac{2p+1}{2p+3}\right]^{1/2} R_{ij} G^{pq}_{ij} ,$$

$$\int \underline{\underline{R}}_{ij} Y_{lm}(\theta,\varphi)\cdot \underline{C}^{*}_{pq}(\theta,\varphi)d\Omega = -iR_{ij} F^{pq}_{ij} ,$$

$$\int (\underline{r}_i\cdot\underline{\underline{R}}_{ij})\underline{A}_{lm}(\theta,\varphi)\cdot \underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = r_i R_{ij}\left(p\left[\frac{2p+3}{2p+1}\right]^{1/2} G^{pq}_{ij} - (p-1)\left[\frac{2p+1}{2p-1}\right]^{1/2} H^{pq}_{ij}\right) ,$$

$$\int (\underline{r}_i\cdot\underline{\underline{R}}_{ij})\underline{A}_{lm}(\theta,\varphi)\cdot \underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{r_i R_{ij}}{\sqrt{(2p+1)(2p+3)}} G^{pq}_{ij} ,$$

$$\int (\underline{r}_i\cdot\underline{\underline{R}}_{ij})\underline{A}_{lm}(\theta,\varphi)\cdot \underline{C}^{*}_{pq}(\theta,\varphi)d\Omega = ir_i R_{ij} F^{pq}_{ij} ,$$

$$\int \underline{r}_i Y_{lm}(\theta,\varphi)\cdot \underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = r_i p\delta_{l,p}\delta_{m,q} ,$$

$$\int \underline{r}_i Y_{lm}(\theta,\varphi)\cdot \underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = -r_i(p+1)\delta_{l,p}\delta_{m,q} ,$$

$$\int \underline{r}_i Y_{lm}(\theta,\varphi)\cdot \underline{C}^{*}_{pq}(\theta,\varphi)d\Omega = 0 .$$

The inner products of the basic solutions $\underline{v}_{lm\sigma}(\underline{r}_j)$, with $\sigma\in\{\alpha,\beta,\gamma\}$, with the vector spherical harmonics $\underline{A}^{*}_{pq}(\theta_i,\varphi_i)$, $\underline{B}^{*}_{pq}(\theta_i,\varphi_i)$ and $\underline{C}^{*}_{pq}(\theta_i,\varphi_i)$ which are different from zero, are for j=i:

$$\int \underline{v}_{lm\alpha}(\underline{r}_i)\cdot \underline{B}^{*}_{pq}(\theta_i,\varphi_i)d\Omega_i = pa_i^{-(p+2)}\delta_{l,p}\delta_{m,q} ,$$

$$\int \underline{v}_{lm\beta}(\underline{r}_i)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = a_i^{-(p+1)}\delta_{l,p}\delta_{m,q}\,,$$

$$\int \underline{v}_{lm\gamma}(\underline{r}_i)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = p(p+1)a_i^{-p}\delta_{l,p}\delta_{m,q}\,,$$

$$\int \underline{v}_{lm\gamma}(\underline{r}_i)\cdot\underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = -\tfrac{1}{2}p(p+1)(2p-1)a_i^{-p}\delta_{l,p}\delta_{m,q}\,,$$

and for j≠i:

$$\int \underline{v}_{lm\alpha}(\underline{r}_j)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = \frac{lp(2p+1)}{(l+1)(2l+1)}a_i^{p-1}\Gamma^{ji}_{lm;pq}\,,$$

$$\int \underline{v}_{lm\beta}(\underline{r}_j)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = \frac{1}{l(l+1)}\sum_{\substack{s\geq 0\\ t}} a_i^{s-1}\Gamma^{ji}_{lm;st}\int(\underline{R}_{ij}\times\underline{A}_{st}(\theta_i,\varphi_i))\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i\,,$$

$$\int \underline{v}_{lm\beta}(\underline{r}_j)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = \frac{p(p+1)}{l(l+1)}a_i^{p}\Gamma^{ji}_{lm;st}$$

$$-\frac{1}{l(l+1)}\sum_{\substack{s\geq 0\\ t}} a_i^{s-1}\Gamma^{ji}_{lm;st}\int(\underline{R}_{ij}\times\underline{A}_{st}(\theta_i,\varphi_i))\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i\,,$$

$$\int \underline{v}_{lm\gamma}(\underline{r}_j)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = p(l+1)a_i^{p+1}\Gamma^{ji}_{lm;pq}$$

$$+(l+1)\sum_{\substack{s\geq 0\\ t}} a_i^{s}\Gamma^{ji}_{lm;st}\int\underline{R}_{ij}Y_{st}(\theta_i,\varphi_i)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i - \tfrac{1}{2}p(2p+1)(l-2)a_i^{p-1}(a_i^2+R_{ij}^2)\Gamma^{ji}_{lm;pq}$$

$$-(l-2)\sum_{\substack{s\geq 0\\ t}} a_i^{s-1}\Gamma^{ji}_{lm;st}\int(\underline{r}_i\cdot\underline{R}_{ij})\underline{A}_{st}(\theta_i,\varphi_i)\cdot\underline{A}^*_{pq}(\theta_i,\varphi_i)d\Omega_i\,,$$

$$\int \underline{v}_{lm\gamma}(\underline{r}_j)\cdot\underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = -(p+1)(l+1)a_i^{p+1}\Gamma^{ji}_{lm;pq}$$

$$+ (l+1)\sum_{\substack{s\geq 0\\ t}} a_i^s\Gamma^{ji}_{lm;st}\int \underline{R}_{ij}Y_{st}(\theta_i,\varphi_i)\cdot\underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i$$

$$-(l-2)\sum_{\substack{s\geq 0\\ t}} a_i^{s-1}\Gamma^{ji}_{lm;st}\int (\underline{r}_i\cdot\underline{R}_{ij})\underline{A}_{st}(\theta_i,\varphi_i)\cdot\underline{B}^*_{pq}(\theta_i,\varphi_i)d\Omega_i\,,$$

$$\int \underline{v}_{lm\gamma}(\underline{r}_j)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i = (l+1)\sum_{\substack{s\geq 0\\ t}} a_i^s\Gamma^{ji}_{lm;st}\int \underline{R}_{ij}Y_{st}(\theta_i,\varphi_i)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i$$

$$-(l-2)\sum_{\substack{s\geq 0\\ t}} a_i^{s-1}\Gamma^{ji}_{lm;st}\int (\underline{r}_i\cdot\underline{R}_{ij})\underline{A}_{st}(\theta_i,\varphi_i)\cdot\underline{C}^*_{pq}(\theta_i,\varphi_i)d\Omega_i\,.$$

Combination of the inner product relations shown at the beginning of this appendix with the inner product relations evaluated above leads to expressions like:

$$n_{11}Y_{1,1}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;s,q+1}\,,\qquad n_{11}Y_{1,-1}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;s,q-1}\,,$$

$$n_{10}Y_{1,0}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;sq}\,.$$

With the definition of $\Gamma^{ji}_{lm;st}$ and the following relations

$$n_{11}Y_{1,1}Y_{lm} = \left[\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}\right]^{1/2}Y_{l+1,m+1} - \left[\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}\right]^{1/2}Y_{l-1,m+1}\,,$$

$$n_{11}Y_{1,-1}Y_{lm} = \left[\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}\right]^{1/2}Y_{l+1,m-1} - \left[\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}\right]^{1/2}Y_{l-1,m-1}\,,$$

$$n_{10}Y_{1,0}Y_{lm} = \left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2} Y_{l+1,m} + \left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{1/2} Y_{l-1,m},$$

we obtain:

$$n_{11}Y_{1,1}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;s,q+1} = \frac{R_{ij}}{(2l+2s+1)}\left[\frac{2s+3}{2s+1}\right]^{1/2}\sqrt{(s-q)(s-q+1)}\,\Gamma^{ji}_{lm;s+1,q}$$

$$-\frac{1}{R_{ij}(2l+2s+1)}\left[\frac{2s-1}{2s+1}\right]^{1/2}\frac{(l+s-m+q)(l+s-m+q+1)}{\sqrt{(s+q)(s+q+1)}}\Gamma^{ji}_{lm;s-1,q},$$

$$n_{11}Y_{1,-1}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;s,q-1} = \frac{R_{ij}}{(2l+2s+1)}\left[\frac{2s+3}{2s+1}\right]^{1/2}\sqrt{(s+q)(s+q+1)}\,\Gamma^{ji}_{lm;s+1,q}$$

$$-\frac{1}{R_{ij}(2l+2s+1)}\left[\frac{2s-1}{2s+1}\right]^{1/2}\frac{(l+s+m-q)(l+s+m-q+1)}{\sqrt{(s-q)(s-q+1)}}\Gamma^{ji}_{lm;s-1,q},$$

$$n_{10}Y_{1,0}(\xi_{ij},\eta_{ij})\Gamma^{ji}_{lm;sq} = -\frac{R_{ij}}{(2l+2s+1)}\left[\frac{2s+3}{2s+1}\right]^{1/2}\sqrt{(s-q+1)(s+q+1)}\,\Gamma^{ji}_{lm;s+1,q}$$

$$-\frac{1}{R_{ij}(2l+2s+1)}\left[\frac{2s-1}{2s+1}\right]^{1/2}\frac{(l+s+m-q)(l+s-m+q)}{\sqrt{(s+q)(s-q)}}\Gamma^{ji}_{lm;s-1,q}.$$

Substitution of these results into the inner product relations of the basic solutions with the vector spherical harmonics leads to the eqs. (2.36)–(2.38).

Appendix II

In this appendix we give an outline of the derivation of the expression of the stresslet $\mathbf{S}_1$, exerted by the fluid on particle 1, in terms of some coefficients, in this case the γ^1_{2m}. We consider two particle hydrodynamic interactions only. The expression is

$$\text{(II.1)} \qquad \mathbf{S}_1 = -\tfrac{3}{2}\eta_0 \sum_{m=-2}^{+2} \gamma^1_{2m}\sigma_{2m}\,,$$

with the tensors σ_{2m} as defined in chapter 2 (eqs. (2.56a)–(2.56c)). We give here a short outline how one can achieve this result for the stresslet $\mathbf{S}_1$. To derive eq. (II.1) we introduce the following integrals, which can be evaluated in a straightforward way. The results are:

$$\text{(II.2)} \quad P[\underline{A}_{lm}] \equiv -\tfrac{1}{2}a^3 \int_{|\underline{r}|=a} (\hat{e}_r \underline{A}_{lm}(\theta,\varphi) + \underline{A}_{lm}(\theta,\varphi)\hat{e}_r - \tfrac{2}{3}I(\underline{A}_{lm}(\theta,\varphi)\cdot\hat{e}_r))d\Omega = -\tfrac{1}{2}a^3\sigma_{2m}\delta_{l,2}\,,$$

with P a shorthand notation for the integral operation. It is obvious that P is a linear operator. Using this notation we have

$$P[\underline{B}_{lm}] = 0\,, \quad P[\underline{C}_{lm}] = 0\,, \quad P[\hat{e}_z \times \underline{A}_{lm}] = \tfrac{1}{4}ima^3\,\sigma_{2m}\delta_{l,2}\,,$$

$$P[Y_{lm}\hat{e}_r] = -\tfrac{1}{10}a^3\sigma_{2m}\delta_{l,2}\,, \quad P[Y_{lm}\hat{e}_z] = -\tfrac{1}{2}a^3\tau_{1m}\delta_{l,1}\,,$$

with

$$\text{(II.3)} \qquad \tau_{1,0} = \frac{1}{\sqrt{15}}\,\sigma_{2,0}\,, \quad \tau_{1,1} = -\tau^*_{1,-1} = \frac{1}{2\sqrt{5}}\,\sigma_{2,1}\,.$$

Furthermore we define the following linear operator (working on the fluid velocity field $\underline{v}(\underline{r})$):

$$Q[\underline{v}(\underline{r})] \equiv -\eta_o\left[\frac{\partial}{\partial r}-\frac{1}{r}\right]\underline{v}(\underline{r})-\frac{\eta_o}{r}\nabla(\underline{r}\cdot\underline{v}(\underline{r}))\,. \tag{II.4}$$

Consequently we write for $\underline{\Pi}_r(\underline{r})$ (see eq. (2.6)):

$$\underline{\Pi}_r(\underline{r}) = p(\underline{r})\hat{e}_r + Q[\underline{v}(\underline{r})]\,, \tag{II.5}$$

and for the stresslet on particle i

$$\mathbf{S}_1 = P[\underline{\Pi}_r(\underline{r})] = P[p(\underline{r})\hat{e}_r] + P[Q[\underline{v}(\underline{r})]]\,. \tag{II.6}$$

There are three sources contributing to $\mathbf{S}_1$, the incoming fluid velocity field $\underline{v}_o(\underline{r})$, which gives the stresslet $\mathbf{S}_1^0$, and the two velocity fields $\underline{v}_1(\underline{r}_1)$ and $\underline{v}_2(\underline{r}_2)$ scattered from both particles, which give $\mathbf{S}_1^1$ and $\mathbf{S}_1^2$ respectively. We first calculate the contribution of the incoming flow field. We can write (see eq. (2.41))

$$Q[\underline{v}_o(\underline{r}_1+\underline{R}_1)] = \sum_{m=-2}^{+2}\alpha^o_{2m}Q[\underline{w}_{2m\alpha}(\underline{r}_1)] + \sum_{m=-1}^{+1}\beta^o_{1m}Q[\underline{w}_{1m\beta}(\underline{r}_1)] + Q[\underline{U}_{o1}]\,. \tag{II.7}$$

The last term of eq. (II.7) equals zero. This is obvious because a constant velocity field is expanded in terms of the basic functions $\underline{w}_{1m\alpha}(\underline{r}_1)$ and $Q[\underline{w}_{1m\alpha}(\underline{r}_1)] = 0$. The final result for eq. (II.7) is

$$Q[\underline{v}_o(\underline{r}_1+\underline{R}_1)] = -2\eta_o\sum_{m=-2}^{+2}\alpha^o_{2m}\underline{A}_{2m}(\theta_1,\varphi_1)\,. \tag{II.8}$$

There is no contribution from the pressure $p_o(\underline{r})$ because all $\gamma^o_{lm}=0$ (see eq. (2.24)). The contribution to the stresslet $\mathbf{S}_1$ is

$$\text{(II.9)} \qquad S_1^0 = -2\eta_o \sum_{m=-2}^{+2} \alpha^o_{2m} P[\underline{A}_{2m}] = \eta_o a^3 \sum_{m=-2}^{+2} \alpha^o_{2m} \sigma_{2m} .$$

In an analogous way, using the expansion in basic solutions of $p_1(\underline{r}_1)$ and $\underline{v}_1(\underline{r}_1)$, we obtain:

$$\text{(II.10)} \qquad S_1^1 = \eta_o \sum_{\substack{l\geq 1 \\ m}} r_1^{-(l+1)} \gamma^1_{lm} \left[l(2l-1) P[Y_{lm}\hat{e}_r] + \frac{(l+1)}{(2l+1)} P[\underline{A}_{lm}] \right]$$

$$= -\tfrac{9}{10}\eta_o \sum_{m=-2}^{+2} \gamma^1_{2m} \sigma_{2m} .$$

In the first sum of this equation we have omitted terms which are zero (see eq. (II.2)). The determination of S_1^2 requires more extensive calculations. First we have to express the pressure $p_2(\underline{r}_2)$ and the fluid velocity $\underline{v}_2(\underline{r}_2)$ in terms of $\underline{r}_1$. This is possible with the Hobson formula and the result is

$$\text{(II.11)} \qquad p_2(\underline{r}_2) = \eta_o \sum_{\substack{l\geq 1 \\ m}} \sum_{\substack{p\geq 0 \\ q}} \frac{n_{pq}}{(p+q)!} l(2l-1) \gamma^2_{lm} M^{21}_{lm;pq} r_1^p Y_{pq}(\theta_1,\varphi_1)$$

$$\text{(II.12)} \qquad \underline{v}_2(\underline{r}_2) = \sum_{\substack{l\geq 1 \\ m}} \sum_{\substack{p\geq 0 \\ q}} \frac{n_{pq}}{(p+q)!} \left[\frac{l}{(l+1)(2l+1)} \alpha^2_{lm} M^{21}_{lm;pq} r_1^{p-1} \underline{A}_{pq}(\theta_1,\varphi_1) \right.$$

$$+ \frac{1}{l(l+1)} \beta^2_{lm} M^{21}_{lm;pq} \left[r_1^p \underline{C}_{pq}(\theta_1,\varphi_1) - r_1^{p-1} (\underline{R}_{12} \times \underline{A}_{pq}(\theta_1,\varphi_1)) \right]$$

$$\left. + (l+1)\gamma^2_{lm} M^{21}_{lm;pq} \left[r_1^p (\underline{r}_1 + \underline{R}_{12}) Y_{pq}(\theta_1,\varphi_1) - \frac{(l-2)}{2(l+1)} r_1^{p-1} (\underline{r}_1 + \underline{R}_{12})^2 \underline{A}_{pq}(\theta_1,\varphi_1) \right] \right] ,$$

where $M^{21}_{lm;pq}$, for the special configuration used in this appendix, is defined in eq. (3.2) and

$\underline{R}_{12}=R\hat{e}_z$. Using both expressions it is not difficult to work out $P[p_2(\underline{r}_1)\hat{e}_r]$ and $P[Q[\underline{v}_2(\underline{r}_1)]]$ although it requires much space. We restrict ourselves to presenting the final result for the stresslet S_1^2. It has the following form:

$$(II.13)\qquad S_1^2 = \eta_o a^3 \sum_{\substack{l\geq 1\\ m}} \sum_{q=-2}^{+2} \frac{n_{2q}}{(2+q)!} M^{21}_{lm;2q} \left[\frac{l}{(l+1)(2l+1)} \alpha^2_{lm} \right.$$

$$\left. + \tfrac{1}{2} iqR \frac{1}{l(l+1)} \beta^2_{lm} + \tfrac{1}{10} a^2 l(2l-1)\gamma^2_{lm} - \tfrac{1}{2} R^2 \frac{(l-q)(l+q)}{(l-2)} \gamma^2_{lm} \right] \sigma_{2q} .$$

This relation for the stresslet S_1^2 can be simplified considerably by comparing it with our set of linear equations, especially with eq. (2.36). If we write down this equation for $p=2$, multiply with $\frac{1}{10}\eta_o a^2 \sigma_{2q}$ and sum over the allowed q values we obtain a final expression that resembles eq. (II.13) so that we can rewrite that equation in the following compact form:

$$(II.14)\qquad S_1^2 = -\eta_o a^3 \sum_{q=-2}^{+2} \alpha^o_{2q} \sigma_{2q} - \tfrac{3}{5}\eta_o \sum_{q=-2}^{+2} \gamma^1_{2q} \sigma_{2q} = -S_1^0 + \tfrac{2}{3} S_1^1 .$$

The final form for the stresslet S_1, exerted by the fluid on particle 1, is now

$$(II.15)\qquad S_1 = S_1^0 + S_1^1 + S_1^2 = -\tfrac{3}{2}\eta_o \sum_{q=-2}^{+2} \gamma^1_{2q} \sigma_{2q} = \tfrac{5}{3} S_1^1 .$$

Appendix III

In this appendix we derive the generalized Hobson formula which we use in chapter 7 section 3. The generalized Hobson formula expresses the "solid spherical harmonic" $\psi^{-}_{lm}(\underline{r})$, defined with respect to the origin O, in terms of the "solid spherical harmonics" $\psi^{+}_{lm}(\underline{r}')$, defined with respect to the origin O'. For the two particle problem it is sufficient to define the z–axis of the coordinate systems O and O' parallel to the line of centers of both particles. Before we give an outline of the proof of the generalized Hobson formula it is important to note that there exists other derivations of the generalized Hobson formula by Danos and Maximon [1] and Felderhof and Jones [2]. These derivations result in a different expression for the generalized Hobson formula as the one derived in this appendix. Both expressions for the generalized Hobson formula should be equivalent. We discuss this point later on in this appendix.

We define the operator $Y_{lm}(\frac{1}{\alpha}\nabla)$ which is related to the spherical harmonics:

$$\cos\theta \longrightarrow \frac{1}{\alpha}\frac{\partial}{\partial z}\ ,\ \sin\theta e^{i\varphi} \longrightarrow \frac{1}{\alpha}\left[\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right]\ ,\ \sin\theta e^{-i\varphi} \longrightarrow \frac{1}{\alpha}\left[\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right]\ ,$$

with $\alpha = \sqrt{-i\omega\rho/\eta_o}$, $\mathrm{Re}(\alpha)\geq 0$. We have to prove of the following two expressions

$$\text{(III.1)} \qquad Y_{lm}(\tfrac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{lm}(\theta,\varphi)g_l(\alpha r)\ ,$$

$$\text{(III.2)} \qquad Y_{lm}(\tfrac{1}{\alpha}\nabla)k_0(\alpha r) = (-1)^l Y_{lm}(\theta,\varphi)k_l(\alpha r)\ .$$

We do not go into the details of the proof of these relations. We only indicate the steps with which one can prove eq. (III.1). The implementation of the steps is straightforward.

- Show: $Y_{00}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{00}(\theta,\varphi)g_0(\alpha r)$;
- Prove by induction: $Y_{l,l}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{l,l}(\theta,\varphi)g_l(\alpha r)$, $\forall l \geq 1$;

- Prove by induction: $Y_{l,-l}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{l,-l}(\theta,\varphi)g_l(\alpha r)$, $\forall l \geq 1$;
- Show: $Y_{l+1,l}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{l+1,l}(\theta,\varphi)g_{l+1}(\alpha r)$, $\forall l \geq 0$;
- Show: $Y_{l+1,-l}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{l+1,-l}(\theta,\varphi)g_{l+1}(\alpha r)$, $\forall l \geq 0$;
- Prove by induction: $Y_{lm}(\frac{1}{\alpha}\nabla)g_0(\alpha r) = Y_{lm}(\theta,\varphi)g_l(\alpha r)$, $\forall l \geq 0$, $|m| \leq l$.

To prove some of these steps one needs recursion relations for the modified spherical Bessel functions $g_l(\alpha r)$ [3] and the Legendre polynomials $P_l^m(\cos\theta)$ [4]. The proof of eq. (III.2) is completely analogous but in that case one needs the recursion relations for the modified spherical Bessel functions $k_l(\alpha r)$ [3].

To express the "solid spherical harmonic" $\psi^-_{lm}(\underline{r})$, defined with respect to the origin O, in terms of the "solid spherical harmonics" $\psi^+_{lm}(\underline{r}')$, defined with respect to the origin O', we need only the addition theorem for Bessel functions applied to $k_0(\alpha r)$ [5]. This addition theorem has the form

$$\text{(III.3)} \qquad k_0(\alpha r) = \sum_{s \geq 0} (-1)^s(2s+1)k_s(\alpha R)P_s(\cos\theta')g_s(\alpha r') \;, \quad |\underline{r}'| < R \;,$$

with R the interparticle distance. Substitution of this result into the expression of $\psi^-_{lm}(\underline{r})$ gives

$$\text{(III.4)} \qquad \psi^-_{lm}(\underline{r}) = (-1)^l Y_{lm}(\tfrac{1}{\alpha}\nabla)\left[\sum_{s \geq 0} (-1)^s(2s+1)k_s(\alpha R)P_s(\tfrac{\partial}{\alpha \partial z'})\right] g_0(\alpha r')$$

$$= (-1)^l \left[\sum_{s \geq 0} (-1)^s(2s+1)k_s(\alpha R)P_s(\tfrac{\partial}{\alpha \partial z'})\right] \psi^+_{lm}(\underline{r}') \;,$$

where we used the equality $\nabla = \nabla'$ if $\underline{R}$ is constant, and eq. (III.1). We can simplify this expression by looking at the following relations:

1) $$(\frac{\partial}{\alpha\partial z'})\psi^+_{lm}(\underline{r}') = \frac{n_{l+1,m}}{n_{lm}}\frac{(l-m+1)}{(2l+1)}\psi^+_{l+1,m}(\underline{r}') + \frac{n_{l-1,m}}{n_{lm}}\frac{(l+m)}{(2l+1)}\psi^+_{l-1,m}(\underline{r}')$$

$$= \sum_{k\geq 0} M^m_{lk}\psi^+_{km}(\underline{r}') ,$$

where

$$M^m_{l,l-1} = \frac{n_{l-1,m}}{n_{lm}}\frac{(l+m)}{(2l+1)}, \quad M^m_{l,l+1} = \frac{n_{l+1,m}}{n_{lm}}\frac{(l-m+1)}{(2l+1)}, \quad l \geq 1$$

and all the other elements of the matrix $\mathbf{M}^m$ are zero.

2) $$(\frac{\partial}{\alpha\partial z'})(\frac{\partial}{\alpha\partial z'})\psi^+_{lm}(\underline{r}') = (\frac{\partial}{\alpha\partial z'})\sum_{k\geq 0} M^m_{lk}\psi^+_{km}(\underline{r}') = \sum_{k\geq 0}[(M^m)^2]_{lk}\psi^+_{km}(\underline{r}') .$$

With these two relations one can prove

$$P_s(\frac{\partial}{\alpha\partial z'})\psi^+_{lm}(\underline{r}') = \sum_{k\geq 0}[P_s(\mathbf{M}^m)]_{lk}\psi^+_{km}(\underline{r}')$$

with $P_s(\mathbf{M}^m)$ a Legendre polynomial with as argument the matrix $\mathbf{M}^m$.

The generalized Hobson formula is now

(III.5) $$\psi^-_{lm}(\underline{r}) = (-1)^l \sum_{k\geq 0}[N^m(\alpha R)]_{lk}\psi^+_{km}(\underline{r}') , \quad |\underline{r}'| < R ,$$

with

$$N^m(\alpha R) = \sum_{s\geq 0}(-1)^s(2s+1)k_s(\alpha R)P_s(\mathbf{M}^m) .$$

In an analogous way,

(III.6) $$\psi^-_{lm}(\underline{r}') = \sum_{k\geq 0}(-1)^k[N^m(\alpha R)]_{lk}\psi^+_{km}(\underline{r}) , \quad |\underline{r}| < R .$$

This result must be equivalent with that obtained by Felderhof and Jones [2]. The equivalence of both results implies (for $m \geq 0$, $l \geq m$ and $k \geq m$)

$$(\text{III.7}) \qquad (-1)^m \sqrt{(2l+1)(2k+1)} \begin{bmatrix} l & k & s \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & k & s \\ -m & m & 0 \end{bmatrix} = [P_s(\mathbf{M}^m)]_{lk},$$

with $\begin{bmatrix} l & k & s \\ 0 & 0 & 0 \end{bmatrix}$ and $\begin{bmatrix} l & k & s \\ -m & m & 0 \end{bmatrix}$ the *3–j* symbols of Wigner [6]. This is supported by numerical evidence where we used the Root–Rational–Fraction package of Stone and Wood to calculate the *3–j* symbols of Wigner [7].

With the derived generalized Hobson formula it is possible to express respectively $\nabla \times \underline{r} \psi^-_{lm}(\underline{r})$ and $\nabla \times (\nabla \times \underline{r} \psi^-_{lm}(\underline{r}))$, defined with respect to O, in terms of the "solid spherical harmonics" defined with respect to O'. The most important steps are ($\nabla = \nabla'$ if the interparticle radius $\underline{R}$ is constant):

$$\nabla \times \underline{r} \psi^-_{lm}(\underline{r}) = (-1)^l (\underline{r}' + \underline{R}) \times \Big(\sum_{k \geq 0} [N^m(\alpha R)]_{lk} \nabla' \psi^+_{km}(\underline{r}') \Big)$$

$$= (-1)^l \sum_{k \geq 0} [N^m(\alpha R)]_{lk} \left[\frac{\alpha}{2k+1} \Big[g_{k-1}(\alpha r') \underline{A}_{km}(\theta', \varphi') - g_{k+1}(\alpha r') \underline{B}_{km}(\theta', \varphi') \Big] \times \underline{R} \right.$$

$$\left. + g_k(\alpha r') \underline{C}_{km}(\theta', \varphi') \right].$$

We have used here the properties of the vector spherical harmonics and the properties of the modified spherical Bessel functions. Furthermore,

$$\nabla \times (\nabla \times \underline{r} \psi^-_{lm}(\underline{r})) = (-1)^l \sum_{k \geq 0} [N^m(\alpha R)]_{lk} \nabla' \times \left[\frac{\alpha}{2k+1} \Big[g_{k-1}(\alpha r') \underline{A}_{km}(\theta', \varphi') - \right.$$

$$\left. g_{k+1}(\alpha r') \underline{B}_{km}(\theta', \varphi') \Big] \times \underline{R} + g_k(\alpha r') \underline{C}_{km}(\theta', \varphi') \right].$$

We can work out the curl operation by using the properties of the spherical harmonics [4] and the properties of the modified spherical Bessel functions [3]. We give here the result only, the calculation is straightforward:

$$\nabla\times(\nabla\times\underline{r}\bar{\psi}_{lm}(\underline{r})) = (-1)^l \sum_{k\geq 0} [N^m(\alpha R)]_{lk}\left[\underline{X}_{km}(\underline{r}',\omega) + \alpha(\underline{R}\cdot\hat{e}_z)\underline{Z}_{km}(\underline{r}',\omega)\right] ,$$

with

$$\text{(III.8)}\quad \underline{X}_{km}(\underline{r}',\omega) = \frac{\alpha}{2k+1}\left[(k+1)g_{k-1}(\alpha r')\underline{A}_{km}(\theta',\varphi') + kg_{k+1}(\alpha r')\underline{B}_{km}(\theta',\varphi')\right] ,$$

$$\begin{aligned}\text{(III.9)}\quad \underline{Z}_{km}(\underline{r}',\omega) = \frac{1}{(2k+1)^2 r'}\Big[&\left[2k^2 g_{k-1}(\alpha r') - (k+1)g_{k+1}(\alpha r')\right]\cos\theta'\underline{A}_{km}(\theta',\varphi') \\ &+ \left[kg_{k-1}(\alpha r') + 2(k+1)^2 g_{k+1}(\alpha r')\right]\cos\theta'\underline{B}_{km}(\theta',\varphi') \\ &+ im(2k+1)\left[g_{k-1}(\alpha r') - g_{k+1}(\alpha r')\right]\underline{C}_{km}(\theta',\varphi') \\ &- \left[(2k^2-1)g_{k-1}(\alpha r') + (k+1)g_{k+1}(\alpha r')\right]\cos\theta'(\underline{A}_{km}(\theta',\varphi')\times\hat{e}_{\varphi'}) \\ &+ \left[kg_{k-1}(\alpha r') - (2(k+1)^2-1)g_{k+1}(\alpha r')\right]\cos\theta'(\underline{B}_{km}(\theta',\varphi')\times\hat{e}_{\varphi'})\Big] \\ &+ \alpha g_k(\alpha r')\sin\theta' Y_{km}(\theta',\varphi')\hat{e}_{\theta'} .\end{aligned}$$

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Appendix IV

In this appendix we show the inner products we need for the determination of the set of linear equations of the coefficients $\{\alpha^i_{lm},\beta^i_{lm},\gamma^i_{lm}\}$. We give here only the results for the inner products.

$$\int \underline{A}_{lm}(\theta,\varphi)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = l(2l+1)\delta_{l,p}\delta_{m,q}\,,$$

$$\int (\underline{A}_{lm}(\theta,\varphi)\times\hat{e}_z)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = im(2l+1)\delta_{l,p}\delta_{m,q}\,,$$

$$\int (\underline{B}_{lm}(\theta,\varphi)\times\hat{e}_z)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = 0\,,$$

$$\int \cos\theta\underline{A}_{lm}(\theta,\varphi)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = (l-1)(l+m)\frac{n_{l-1,\,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$+\, l(l+m+1)\frac{n_{lm}}{n_{l+1,\,m}}\delta_{l,p-1}\delta_{m,q}\,,$$

$$\int \cos\theta\underline{B}_{lm}(\theta,\varphi)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = -\frac{(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,\,m}}\delta_{l,p-1}\delta_{m,q}\,,$$

$$\int (\sin\theta\underline{A}_{lm}(\theta,\varphi)\times\hat{e}_\varphi)\cdot\underline{A}^*_{pq}(\theta,\varphi)d\Omega = -(l-1)(l+m)\frac{n_{l-1,\,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$+\, l(l+m+1)\frac{n_{lm}}{n_{l+1,\,m}}\delta_{l,p-1}\delta_{m,q}\,,$$

$$\int (\sin\theta \underline{B}_{lm}(\theta,\varphi)\times\hat{e}_{\varphi})\cdot\underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{-2(l+1)(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int \sin\theta Y_{lm}(\theta,\varphi)\hat{e}_{\theta}\cdot\underline{A}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{(l-1)(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$-\frac{(l+2)(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int \underline{B}_{lm}(\theta,\varphi)\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = (l+1)(2l+1)\delta_{l,p}\delta_{m,q},$$

$$\int (\underline{A}_{lm}(\theta,\varphi)\times\hat{e}_{z})\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = 0,$$

$$\int (\underline{B}_{lm}(\theta,\varphi)\times\hat{e}_{z})\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = -im(2l+1)\delta_{l,p}\delta_{m,q},$$

$$\int \cos\theta \underline{A}_{lm}(\theta,\varphi)\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = -\frac{(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q},$$

$$\int \cos\theta \underline{B}_{lm}(\theta,\varphi)\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{(l+1)(l+m)(2l-1)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$+\frac{(l+2)(l+m+1)(2l+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int (\sin\theta \underline{A}_{lm}(\theta,\varphi)\times\hat{e}_{\varphi})\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{2l(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q},$$

$$\int (\sin\theta \underline{B}_{lm}(\theta,\varphi)\times\hat{e}_{\varphi})\cdot\underline{B}^{*}_{pq}(\theta,\varphi)d\Omega = \frac{(l+1)(l+m)(2l-1)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$-\frac{(l+2)(l+m+1)(2l+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int \sin\theta Y_{lm}(\theta,\varphi)\hat{e}_\theta\cdot\underline{B}^*_{pq}(\theta,\varphi)d\Omega=\frac{(l-1)(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$-\frac{(l+2)(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int \underline{C}_{lm}(\theta,\varphi)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=l(l+1)\delta_{l,p}\delta_{m,q},$$

$$\int (\underline{A}_{lm}(\theta,\varphi)\times\hat{e}_z)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=(l-1)(l+m)\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q},$$

$$\int (\underline{B}_{lm}(\theta,\varphi)\times\hat{e}_z)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=\frac{(l+2)(l+m+1)(2l+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q},$$

$$\int \cos\theta\underline{A}_{lm}(\theta,\varphi)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=-im\delta_{l,p}\delta_{m,q},$$

$$\int \cos\theta\underline{B}_{lm}(\theta,\varphi)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=-im\delta_{l,p}\delta_{m,q},$$

$$\int (\sin\theta\underline{A}_{lm}(\theta,\varphi)\times\hat{e}_\varphi)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=iml\delta_{l,p}\delta_{m,q},$$

$$\int (\sin\theta\underline{B}_{lm}(\theta,\varphi)\times\hat{e}_\varphi)\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=-im(l+1)\delta_{l,p}\delta_{m,q},$$

$$\int \sin\theta Y_{lm}(\theta,\varphi)\hat{e}_\theta\cdot\underline{C}^*_{pq}(\theta,\varphi)d\Omega=-im\delta_{l,p}\delta_{m,q}.$$

With the help of the inner products mentioned above and the vector functions $\underline{X}_{lm}(\underline{r},\omega)$ and $\underline{Z}_{lm}(\underline{r},\omega)$ defined in appendix III (respectively eq. (III.8) and (III.9)) we can determine the following inner products:

$$\int \underline{X}_{lm}(\underline{r},\omega)\cdot\underline{A}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = l(l+1)\alpha g_{l-1}(\alpha r)\delta_{l,p}\delta_{m,q}\,,$$

$$\int \underline{X}_{lm}(\underline{r},\omega)\cdot\underline{B}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = l(l+1)\alpha g_{l+1}(\alpha r)\delta_{l,p}\delta_{m,q}\,,$$

$$\int \underline{X}_{lm}(\underline{r},\omega)\cdot\underline{C}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = 0\,,$$

$$\int \underline{Z}_{lm}(\underline{r},\omega)\cdot\underline{A}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = \alpha g_{l-2}(\alpha r)\frac{(l-1)(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$-\alpha g_{l}(\alpha r)\frac{(l+2)(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q}\,,$$

$$\int \underline{Z}_{lm}(\underline{r},\omega)\cdot\underline{B}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = \alpha g_{l}(\alpha r)\frac{(l-1)(l+m)}{(2l+1)}\frac{n_{l-1,m}}{n_{lm}}\delta_{l,p+1}\delta_{m,q}$$

$$-\alpha g_{l+2}(\alpha r)\frac{(l+2)(l+m+1)}{(2l+3)}\frac{n_{lm}}{n_{l+1,m}}\delta_{l,p-1}\delta_{m,q}\,,$$

$$\int \underline{Z}_{lm}(\underline{r},\omega)\cdot\underline{C}^{*}_{pq}(\theta,\varphi)\mathrm{d}\Omega = -im\alpha g_{l}(\alpha r)\delta_{l,p}\delta_{m,q}\,.$$

Appendix V

The calculation of the integrals needed for the determination of eqs. (7.42) and (7.43) for the force $\underline{F}_i(\omega)$ and torque $\underline{T}_i(\omega)$ respectively can be performed with the help of the following integrals, where we show the nonzero integrals only:

$$\int p_{lm\alpha}(\underline{r},\omega)\hat{e}_r d\Omega = \frac{\eta_o}{2l+1} r^{-(l+1)} \int Y_{lm}(\theta,\varphi)\hat{e}_r d\Omega ,$$

$$\int \underline{v}_{lm\gamma}(\underline{r},\omega)d\Omega = \frac{2\alpha}{\pi l(2l+1)} k_{l-1}(\alpha r) \int \underline{A}_{lm}(\theta,\varphi)d\Omega ,$$

$$\int \nabla(\underline{r}\cdot\underline{v}_{lm\gamma}(\underline{r},\omega))d\Omega = \frac{2\alpha}{\pi(2l+1)} k_{l-1}(\alpha r) \int \underline{A}_{lm}(\theta,\varphi)d\Omega ,$$

$$\int (\hat{e}_r \times \underline{v}_{lm\beta}(\underline{r},\omega))d\Omega = \frac{2\alpha}{\pi l(l+1)} k_l(\alpha r) \int (\hat{e}_r \times \underline{C}_{lm}(\theta,\varphi))d\Omega .$$

Substitution of these integrals into eq. (7.41) leads to

$$\underline{F}_i(\omega) = -\frac{\eta_o}{6}\left[n_{11}(\alpha^i_{1,-1}(\omega)-\alpha^i_{1,1}(\omega))\hat{e}_x - in_{11}(\alpha^i_{1,-1}+\alpha^i_{1,1}(\omega))\hat{e}_y + 2n_{10}\alpha^i_{1,0}(\omega)\hat{e}_z\right]$$

$$-\frac{\eta_o\alpha^2a^2}{\pi} k_1(\alpha a)\left[n_{11}(\gamma^i_{1,-1}(\omega)-\gamma^i_{1,1}(\omega))\hat{e}_x - in_{11}(\gamma^i_{1,-1}+\gamma^i_{1,1}(\omega))\hat{e}_y\right.$$

$$\left. +2n_{10}\gamma^i_{1,0}(\omega)\hat{e}_z\right] + \eta_o\alpha^2 \int_{|\underline{r}_i|\le a} \underline{v}_j(\underline{r}_i+\underline{R}_{ij},\omega)d\underline{r}_i ,$$

where $j\neq i$. We can simplify this complicated expression by considering the following expression:

$$\frac{4\pi\eta_o a}{3}\alpha^2 a^2 \underline{U}_i(\omega) = -\frac{\eta_o \alpha^2 a^3}{6}\Bigg[n_{11}(\hat{e}_x + i\hat{e}_y)\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot(\underline{A}^*_{1,1}(\theta_i,\varphi_i) - \underline{B}^*_{1,1}(\theta_i,\varphi_i))d\Omega_i$$

$$- n_{11}(\hat{e}_x - i\hat{e}_y)\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot(\underline{A}^*_{1,-1}(\theta_i,\varphi_i) - \underline{B}^*_{1,-1}(\theta_i,\varphi_i))d\Omega_i$$

$$- 2n_{10}\hat{e}_z\int_{|\underline{r}_i|=a} \underline{v}^i(\underline{r}_i,\omega)\cdot(\underline{A}^*_{1,0}(\theta_i,\varphi_i) - \underline{B}^*_{1,0}(\theta_i,\varphi_i))d\Omega_i\Bigg] .$$

We can rewrite the r.h.s. of this expression by using the set of linear equations derived in section 3 of chapter 7. After rearrangement we obtain:

$$\frac{\eta_o \alpha^2 a^2}{\pi} k_1(\alpha a)\Big[n_{11}(\gamma^i_{1,-1}(\omega) - \gamma^i_{1,1}(\omega))\hat{e}_x - in_{11}(\gamma^i_{1,-1} + \gamma^i_{1,1}(\omega))\hat{e}_y + 2n_{10}\gamma^i_{1,0}(\omega)\hat{e}_z\Big]$$

$$+ \eta\alpha^2\int_{|\underline{r}_i|\le a} \underline{v}_j(\underline{r}_i + \underline{R}_{ij},\omega)d\underline{r}_i = \frac{4\pi\eta_o a}{3}\alpha^2 a^2 \underline{U}_i(\omega)$$

$$- \frac{\eta_o}{3}\Big[n_{11}(\alpha^i_{1,-1}(\omega) - \alpha^i_{1,1}(\omega))\hat{e}_x - in_{11}(\alpha^i_{1,-1} + \alpha^i_{1,1}(\omega))\hat{e}_y + 2n_{10}\alpha^i_{1,0}(\omega)\hat{e}_z\Big] ,$$

where $j \neq i$. After combination of this result with the equation of $\underline{F}_i(\omega)$ we obtain the final expression (eq. (7.42)).

Summary

The research presented in this thesis concernes a study of the effects of both quasistatic as retarded hydrodynamic interactions among spherical particles in a suspension, on some transport coefficients. It is a theoretical study with a numerical component.

The first chapter is a short introduction without details. Some attention has been paid to the development of simulation experiments. Some results of these simulation experiments have been used to compare our findings with. In addition the underlying motivation for this research has been expounded.

In chapter 2 the problem of N hydrodynamically interacting spheres, present in an unbounded fluid with an externally imposed flow, is studied within the quasistatic limit (Stokes limit). On basis of the linearity of the Navier–Stokes equations a scattered fluid velocity field around each sphere is introduced and that velocity field can be expanded with the help of a complete set of basic functions. The problem of N interacting spheres is reformulated in terms of a set of linear equations of the expansion coefficients. Then the force, torque and stresslet are expressed in terms of some expansion coefficients. The combination of both results leads to the determination of the components of the grand mobility matrix. The transport coefficients can be studied with it. In the next chapter the method is compared with findings from the literature concerning the two particle problem, which is intensively studied in the past. In the first place the convergence behaviour of the components of the grand mobility matrix is studied and it is shown that the presented method results in a faster and more systematic convergence behaviour of these components. This is especially important for the study of three and more particle interactions. The virial expansions of the translational and rotational self–diffusion coefficient and of the translational and rotational sedimentation velocity are determined. The result for the rotational sedimentation is new.

In the fourth chapter an alternative approach is presented to determine the effective viscosity of a hard sphere suspension by using a method introduced by Saito in the early fifties. The set of linear equations presented in chapter 2 is appropriate. The final result for the effective viscosity agrees very well with both experimental results and simulation data up to high volume fractions of dispersed particles, although binary interactions are included only. At high volume fractions it is necessary to include three and more particle hydrodynamic interactions in the expression for the effective viscosity, but this seems to lead to subtle corrections in contrast to the commonly used methods.

In chapter 5 a study of three particle hydrodynamic interactions is presented. The results for some special configurations are compared with results available in the literature. From this comparison it is evident that with the presented method, three particle interactions can be studied very satisfactorily. On top of that the virial expansions of transport coefficients mentioned before are improved by including three particle hydrodynamic interactions. These results are new. The transport coefficients related to rotational properties are described very well up to $\varphi \approx 0.4$ if compared with simulation data. The virial expansion for the translational self–diffusion coefficient disagrees with some earlier expressions, but our expression resembles recent experimental results up to $\varphi \approx 0.4$. Sedimentation is difficult to describe with a virial expansion, but the expression presented in this thesis is an improvement.

The aim of chapter 6 is twofold. In the first place it is an introduction to the theory of Brownian motion based on the Stokes–Boussinesq equation. The correlation functions of the Brownian particles are studied on basis of a generalized Langevin equation. The free Brownian particle is treated. The mathematical tools introduced appear to be useful also in two other cases: the Brownian particle in a harmonic potential and in a shear flow. The results are only valid in the case that hydrodynamic interactions can be neglected, thus in case of very low volume fraction of dispersed particles. In chapter 7 these retarded hydrodynamic interactions are included. It is assumed that there is no externally imposed

flow field. It proved to be possible to calculate the components of the grand mobility matrix, including two particle hydrodynamic interactions, and, with some of these components, the velocity autocorrelation function and time dependent diffusion coefficient of the Brownian particles.

In chapter 8 the most important conclusions are summarized and some possible future applications of the presented method are listed.

Samenvatting

Het in dit proefschrift beschreven onderzoek betreft de effecten van zowel quasistatische als geretardeerde hydrodynamische wisselwerking tussen bolvormige deeltjes in een suspensie, op een aantal transportcoëfficiënten. Het is theoretisch van aard en heeft daarnaast een numerieke component.

Het eerste hoofdstuk dient als een korte inleiding zonder details. Enige aandacht wordt besteed aan simulatie experimenten. Een aantal resultaten van deze simulatie experimenten vormen belangrijk vergelijkingsmateriaal voor door ons gepresenteerde resultaten. Tevens wordt de onderliggende motivatie voor dit onderzoek uiteengezet.

In hoofdstuk 2 wordt het probleem bestudeerd van N hydrodynamisch wisselwerkende bollen, aanwezig in een oneindig uitgestrekte vloeistof met een extern opgelegd stromingsveld, in de quasistatische limiet (Stokes limiet). Vanwege de lineariteit van de Navier–Stokes vergelijkingen kan een verstrooid vloeistofveld rond iedere bol geintroduceerd worden en dat vloeistofveld kan ontwikkeld worden met behulp van een compleet set basisfuncties. Het probleem van N wisselwerkende bollen wordt gereformuleerd in termen van een stelsel lineaire vergelijkingen voor de expansiecoëfficiënten. Daarna worden de kracht, het krachtmoment en de stresslet uitgedrukt in termen van een aantal expansiecoëfficiënten. Combinatie van beide resultaten maakt het mogelijk om de componenten van de mobiliteitsmatrix te bepalen, waarmee de transportcoëfficiënten onderzocht kunnen worden. De methode wordt in het daarop volgende hoofdstuk uitgebreid vergeleken met resultaten uit de literatuur betreffende het twee deeltjes probleem dat reeds in het verleden intensief bestudeerd is. In eerste instantie wordt het convergentiegedrag van de componenten van de mobiliteitsmatrix onderzocht en het blijkt dat de gepresenteerde methode tot snellere en meer systematisch convergentiegedrag van deze componenten leidt. Dit is vooral van belang als drie en meer deeltjes wisselwerking bestudeerd wordt. De viriaalontwikkelingen van de translatie en

rotatie zelfdiffusiecoëfficiënt en van de translatie en rotatie sedimentatie snelheid zijn bepaald. Het resultaat van de rotatie sedimentatie is nieuw.

Het vierde hoofdstuk is geheel gewijd aan een alternatieve manier om de effectieve viscositeit van een harde bollen suspensie te bepalen volgens een methode geintroduceerd door Saito in het begin van de jaren vijftig. Het in hoofdstuk 2 geformuleerde stelsel lineaire vergelijkingen is hiertoe geschikt. Het uiteindelijke resultaat voor de effectieve viscositeit komt goed overeen, tot hoge volumefracties van gedispergeerde deeltjes, met zowel experimentele resultaten als simulatie data, alhoewel slechts binaire wisselwerking is meegenomen. Bij hoge volumefracties is het noodzakelijk om drie en meer deeltjes wisselwerking mee te nemen in de uitdrukking voor de effectieve viscositeit, maar klaarblijkelijk leidt dit slechts tot subtiele correcties in tegenstelling tot de gewoonlijk gebruikte methodes.

In hoofdstuk 5 is een studie naar drie deeltjes wisselwerking gepresenteerd. De resultaten voor een aantal speciale configuraties zijn vergeleken met enkele resultaten uit de literatuur. Uit deze vergelijking blijkt dat de gepresenteerde methode goed voldoet om drie deeltjes wisselwerking te bestuderen. Daarnaast zijn de al eerder genoemde resultaten voor viriaalontwikkelingen van een aantal transportcoëfficiënten gecorrigeerd door drie deeltjes wisselwerking mee te nemen. Deze resultaten zijn nieuw. De transportcoëfficiënten gerelateerd aan rotaties worden goed beschreven tot $\varphi \approx 0.4$ als ze vergeleken worden met simulatie experimenten. De viriaalontwikkeling voor de translatie zelfdiffusiecoëfficiënt wijkt af van eerdere uitdrukkingen, maar onze uitdrukking voldoet goed tot $\varphi \approx 0.4$ vergeleken bij met recente experimenten. Het is moeilijk om sedimentatie te beschrijven met een viriaalontwikkeling maar de in dit proefschrift gepresenteerde uitdrukking is desondanks een verbetering.

Het zesde hoofdstuk heeft een tweeledig doel. Ten eerste dient het als een inleiding in de theorie van de Brownse beweging waarbij de Stokes–Boussinesq vergelijking als basis dient. De correlatiefuncties van het Brownse deeltje zijn onderzocht op grond van een

gegeneraliseerde Langevin vergelijking. Het vrije Brownse deeltje wordt bestudeerd. De gebruikte wiskundige methoden blijken ook nuttig te zijn in twee andere gevallen: een Browns deeltje in een harmonische potentiaal en in een afschuifstroming. Deze resultaten gelden alleen als de hydrodynamische wisselwerking tussen de Brownse deeltjes verwaarloosbaar is, d.w.z. bij zeer lage volumefracties van gedispergeerde deeltjes. In hoofdstuk 7 wordt deze hydrodynamische wisselwerking meegenomen. Er wordt aangenomen dat er geen uitwendig stromingsveld is opgelegd. Het blijkt mogelijk te zijn de componenten van de mobiliteits matrix te bepalen, waarbij twee deeltjes wisselwerking is meegenomen, en aan de hand daarvan de snelheids autocorrelatie functie en tijdafhankelijke diffusiecoëfficiënt van de Brownse deeltjes.

In hoofdstuk 8 worden de belangrijkste conclusies samengevat en worden enige mogelijke toekomstige toepassingen van de gepresenteerde methode opgesomd.

Curriculum Vitae

Herman Clercx werd op 1 februari 1961 geboren te Bussum. Na verhuisd te zijn naar het zuiden van het land bezocht hij de lagere school in Rijen en daarna van 1973 tot 1979 het John F. Kennedy atheneum te Dongen. In 1979 begon hij met een studie natuurkunde aan de Katholieke Universiteit Nijmegen.

Nadat in 1983 het kandidaatsexamen was behaald koos hij voor de afstudeerrichting theoretische natuurkunde. In dit kader vond het afstudeeronderzoek bij prof.dr. G.Vertogen plaats, het omvatte een studie naar de indirecte wisselwerking tussen magnetische onzuiverheden in een electronengas. In augustus 1987 behaalde hij cum laude het doctoraalexamen. In september van dat jaar begon hij bij de vakgroep transportfysica onder leiding van prof.dr.ir. P.P.J.M. Schram aan het in dit proefschrift beschreven onderzoek.

Dankwoord

Hierbij wil ik iedereen bedanken die hun medewerking hebben verleend aan het tot stand komen van dit proefschrift. In het bijzonder wil ik noemen:

- mijn promotor en begeleider van het onderzoek, prof.dr.ir. P.P.J.M. Schram. Hij heeft mij een grote vrijheid gelaten in het onderzoek, wat ik zeer heb gewaardeerd, en was altijd beschikbaar voor stimulerende discussies. De prettige samenwerking hebben mij de afgelopen vier jaar veel voldoening in het onderzoek gebracht.
- mijn partner Adriek, die de laatste maanden voor het tot stand komen van het proefschrift met mij kon samenleven terwijl ik slechts zelden achter het beeldscherm vandaan kwam.
- mijn promotor prof.dr. B.U. Felderhof, die heeft bijgedragen aan het tot stand komen van dit proefschrift door middel van vele nuttige opmerkingen en aanwijzingen.
- mevr. M.W.J. de Man–Vrehen. Zij heeft vele uren besteed aan een taalkundige verbetering van het manuscript van dit proefschrift.

Stellingen bij het proefschrift van H.J.H. Clercx, 22 oktober 1991.

1 Het toepassen van lubricatietheorie in de studie van het gedrag van suspensies is niet relevant omdat deze theorie slechts geldig zou zijn voor deeltjesafstanden, die toepassing van hydrodynamische theorieën niet toelaten.

D.J. Jeffrey en Y. Onishi, J. Fluid Mech. 139 (1984) 261.

S. Kim en R.T. Mifflin, Phys. Fluids 28 (1985) 2033.

2 Het in dit proefschrift gepresenteerde stelsel lineaire algebraïsche vergelijkingen, noodzakelijk om de N–deeltjes mobiliteitsmatrix te bepalen, is opgebouwd uit twee deeltjes wisselwerkingstermen. Oplossen van dit stelsel leidt tot een N–deeltjes weerstandsmatrix met meer deeltjes wisselwerkingstermen. Hiermee kan worden aangetoond dat de bewering van Durlofsky, Brady en Bossis inhoudende dat inversie van hun N–deeltjes mobiliteitsmatrix, met slechts paarwisselwerkingstermen, leidt tot een weerstandsmatrix met meer deeltjes wisselwerkingstermen, in principe correct is.

Dit proefschrift, hoofdstuk 2.

L. Durlofsky, J.F. Brady en G. Bossis, J. Fluid Mech. 180 (1987) 21.

3 In een oneindig uitgestrekt colloïdaal kristal, waarin ieder bolvormig deeltje zich bevindt op een roosterpunt en dezelfde omgeving ziet, is de rotatiezelfdiffusiecoëfficiënt ongevoelig voor de hydrodynamische wisselwerking in het colloïdaal kristal. Dit is geldig voor elke willekeurige roosterparameter, waarbij vanzelfsprekend wordt aangenomen dat de roosterparameter niet kleiner kan worden dan tweemaal de deeltjesstraal.

4 Het totale hydrodynamische N–deeltjes probleem in een oneindig uitgestrekt colloïdaal kristal, waarin ieder bolvormig deeltje zich bevindt op een roosterpunt en dezelfde omgeving ziet, is te herformuleren in termen van vrije quasi–deeltjes.

5 Om snelheidsautocorrelatiefuncties van Brownse deeltjes te verkrijgen die in gedrag lijken op deze functies verkregen m.b.v. moleculaire dynamica berekeningen aan harde bollen vloeistoffen, is het essentieel om op zijn minst binaire geretardeerde hydrodynamische wisselwerking tussen de Brownse deeltjes te beschouwen. De zelf–interactie van één Browns deeltje via de vloeistofmoleculen is niet voldoende.

Zie bijvoorbeeld: J.P. Hansen en I.R. McDonald, Theory of simple liquids (Academic Press, London, 1986), hoofdstuk 8.

Dit proefschrift, hoofdstuk 7.

6 De niet–evenwicht statistische operator van Zubarev is bij de berekening van het electrische geleidingsvermogen van plasma's alleen bruikbaar voor stationaire velden. Dit wijst op een ernstige beperking van de geldigheid van het Zubarev–formalisme.

G. Ropke en F.E. Hohne, Phys. Stat. Sol. (b) 107 (1981) 603.

H.H. Brouwer en P.P.J.M. Schram, Physica A 141 (1987) 589.

7 Het verdient aanbeveling om verslaggevers, die op de televisie rechtstreeks wielerwedstrijden verslaan, tegelijkertijd met iedere ravitaillering van de wielrenners concentratieverhogende middelen toe te dienen opdat de televisiekijker tot de finish van de wielerwedstrijd verschoond blijft van onzinnige en foutieve opmerkingen van de verslaggevers.

8 Zolang slechts een kleine minderheid van de huishoudens in Nederland gebruik maakt van een zogenaamde anti–reclamedrukwerk–sticker zal het effect van deze sticker contraproductief zijn, daar milieubewuste huishoudens beter in staat zijn dat reclamedrukwerk in het oud papier circuit te brengen dan de bezorgers ervan. Deze laatsten hebben nogal eens de vervelende gewoonte om het overblijvend reclamedrukwerk te deponeren op plaatsen waar het niet thuis hoort.

9 Het is bevreemdend dat in kringen van de middenstand nogal eens kritische geluiden te horen zijn over de hoogte van sociale uitkeringen. De middenstanders dienen zich te realiseren dat zij, net als de personen die een sociale uitkering ontvangen, belanghebbend zijn.

10 In een artikel van Widom wordt de bewegingsvergelijking voor de snelheidsauto–correlatiefunctie $\phi(t)$ van een Browns deeltje afgeleid m.b.v. lineaire responsie–theorie. Ten onrechte wordt daarbij de beginvoorwaarde $\phi(0)=k_B T/m$ (k_B: constante van Boltzmann, T: absolute temperatuur, m: massa van het deeltje) opgelegd. De lineaire responsie–theorie levert zelf de beginvoorwaarde, en wel $\phi(0)=k_B T/(m+\frac{1}{2}m_0)$, waarin m_0 de verplaatste vloeistofmassa is.

A. Widom, Phys. Rev. A 3 (1971) 1394.