ON TRANSPORT PROPERTIES OF CONCENTRATED SUSPENSIONS

C.W.J. BEENAKKER

STELLINGEN

1. Uit het Rotne-Prager variatieprincipe voor hydrodynamische mobiliteiten volgt voor de (korte-tijd) collectieve diffusiecoëfficiënt D_c van gesuspendeerde bolvormige deeltjes de ongelijkheid:

   $$D_c \leqslant D_o[\tfrac{1}{2}\pi a G(0)]^{-1} \int_0^\infty dk\ G(k)k^{-2}\sin^2 ak,$$

   waarbij D_o de Stokes-Einstein constante aanduidt, a de straal van de deeltjes en G(k) hun structuurfunctie.

   J. Rotne en S. Prager, J.Chem.Phys. 50 (1969) 4831.

2. Beide door Stauffer en Clavin voorgestelde uitbreidingen van Batchelor's sedimentatie theorie naar het geconcentreerde regime impliceren voor de diffusiecoëfficiënt een ernstige schending van bovenstaande ongelijkheid.

   D. Stauffer en P. Clavin, J.Physique L42 (1981) 353.

3. Ten onrechte menen Ermak en McCammon dat hun algoritme voor simulatie van Brownse beweging in suspensies verschilt van het algoritme dat zou volgen uit de door Zwanzig geformuleerde Langevin vergelijking voor dit proces.

   D.L. Ermak en J.A. McCammon, J.Chem.Phys. 69 (1978) 1352.

4. De divergentie van de sedimentatiesnelheid in een onbegrensde suspensie treedt niet op indien de invloed van de wand die de suspensie draagt in rekening wordt gebracht.

   C.W.J. Beenakker en P. Mazur, te verschijnen.

5. Door Baas e.a. wordt de door hen waargenomen afname van stromings dubbele breking in gassen bij hogere drukken toegeschreven aan een afbuiging van de gebruikte laserstraal ten gevolge van variaties in de dichtheid. Veeleer is het optreden van hydrodynamische instabiliteiten de oorzaak van dit verschijnsel.

   F. Baas, J.N. Breunese, H.F.P. Knaap en J.J.M. Beenakker,
   Physica 88A (1977) 1.

6. De formule

   $$\{f(x,k),g(x,k)\} = \sum_{n=1}^{\infty} \frac{1}{n!}\left[\left(\frac{\partial^n}{\partial x^n} f\right)\left(\frac{\partial^n}{\partial k^n} g\right) - \left(\frac{\partial^n}{\partial x^n} g\right)\left(\frac{\partial^n}{\partial k^n} f\right)\right]$$

   kan beschouwd worden als de definitie van een gegeneraliseerd Poisson haakje $\{f,g\}$.

7. De wiskundige formulering van één-dimensionale stroming door poreuse media geeft een randwaarde probleem met een zogenaamde vrije rand, die verzadigde en onverzadigde gebieden scheidt. Met een door J. Hulshof ontwikkelde methode kan men de continuïteit van deze vrije rand (als kromme in het ruimte-tijd vlak) bewijzen onder ruimere voorwaarden dan vereist door van Duyn.

C.J. van Duyn, Arch. for Rat.Mech. and Analysis, 79 (1982) 261.

8. Ten onrechte geven Prosperetti en Plesset geen rechtvaardiging voor de veronderstelling van een continu temperatuurverloop in de verdampende vloeistof die zij bestuderen.

A. Prosperetti en M.S. Plesset, Phys.Fluids 27 (1984) 2590.

9. De excessieve smeltdrukverlaging van gepolariseerd ^{3}He, waargenomen door Bonfait e.a. en door hen toegeschreven aan een systematische fout in de metingen van de magnetisatie, kan beschouwd worden als een experimentele aanwijzing voor de geringe magnetische susceptibiliteit van dit systeem - in overeenstemming met de theorie van Bedell en Quader.

G. Bonfait, L. Puech, A.S. Greenberg, G. Eska, B. Castaing en D. Thoulouze, Proc.17th Int.Conf. on Low Temperature Physics (Elsevier, 1984): blz. 481.
K.S. Bedell en K.F. Quader, Phys.Lett. 96A (1983) 91.

10. Als instrument voor de meting van zeer korte laserpulsen verdient een drie-armige intensiteits interferometer de voorkeur boven een twee-armige.

B. Wirnitzer, Opt.Commun. 48 (1983) 225.

11. De Willibrord vertaling van Jesaja 7,14 weerspiegelt een verandering in de Nederlandse mariologie.

C.W.J. Beenakker

Leiden, 28 november 1984

ON TRANSPORT PROPERTIES OF CONCENTRATED SUSPENSIONS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE WISKUNDE EN NATUURWETENSCHAPPEN
AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG
VAN DE RECTOR MAGNIFICUS DR. A.A.H. KASSENAAR,
HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE,
VOLGENS BESLUIT VAN HET COLLEGE VAN DEKANEN
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Carlo Willem Joannes Beenakker

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Prof.dr. J. Schmidt

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aan mijn ouders
aan Mayke en Jan-Willem

CONTENTS

CHAPTER I

INTRODUCTION

1. Preface

Transport properties of suspensions of macroscopic particles in a viscous fluid are concentration dependent due to direct interactions between the particles, as well as due to a coupling of their motion via the fluid[1]. This coupling is called *hydrodynamic interaction*. To understand the influence of hydrodynamic interactions on properties of suspensions has been the motivation of the work described in this thesis.

Both from a theoretical and experimental point of view, the influence of hydrodynamic interactions is best studied in the absence of any long-ranged (e.g. electromagnetic) direct interactions between the particles. For this reason we shall restrict our attention to systems where the suspended particles have of themselves only the short-ranged interaction of hard spheres. Such suspensions can be realized in the laboratory: van Helden and Vrij[2], notably, have developed a system of silica particles which in a nonpolar solvent interact as hard spheres over a broad concentration range, as is borne out by measurements of the osmotic compressibility. Studies of these, and other, "hard-sphere" suspensions have yielded much information on the effect of hydrodynamic interactions as the suspension becomes more and more concentrated. Theoretical investigations, on the contrary, have been restricted mainly to the low-density regime, where it is sufficient to consider only the hydrodynamic interactions of pairs of particles. Difficulties in accounting for non-pairwise additive contributions to these interactions hampered an extension to suspensions which are not dilute. Significantly, the section on hydrodynamic interactions in a 1980 review[1c] concludes with the discouraging observation that "the intractability of the three-body hydrodynamic interaction problem forces us to hope that [the assumption of pairwise additivity of the hydrodynamic couplings] holds in more concentrated suspensions as well [as in dilute suspensions]". In the past few years, however, important advances have been made towards a solution of the many-sphere interaction problem, which have improved considerably the outlook for an understanding of the properties of concentrated suspensions and which have formed the basis of the work described in this thesis. As a background for the following chapters we shall now consider the hydrodynamic problem in more detail.

2. Many-sphere hydrodynamic interactions

For our purposes, the motion of the fluid is described to a sufficient accuracy by the static, linearized Navier-Stokes equation for an incompressible fluid*

$$-\eta\Delta\vec{v} + \vec{\nabla}p = 0, \quad \vec{\nabla}\cdot\vec{v} = 0, \tag{1}$$

where $\vec{v}(\vec{r},t)$ and $p(\vec{r},t)$ are the velocity and pressure fields and η is the (kinematic) viscosity of the fluid. Eq. (1), valid within the fluid, is supplemented by a stick boundary condition on the surface of each sphere $i = 1,2,\ldots N$,

$$\vec{v} = \vec{u}_i + \vec{\omega}_i \wedge (\vec{r} - \vec{R}_i) \quad \text{for } |\vec{r} - \vec{R}_i| = a. \tag{2}$$

Here $\vec{u}_i(t)$ and $\vec{\omega}_i(t)$ are the velocity and angular velocity of sphere i, with radius a and centre at $\vec{R}_i(t)$.

The solution of these socalled "creeping flow" equations has been the subject of many investigations[3]. Important quantities to be determined are the mobility tensors $\underline{\mu}_{ij}$, which relate the velocity of sphere i to the force $\vec{K}_j$ exerted by the fluid on each sphere j,

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*The static approximation, in particular, limits the validity of the analysis to time scales large compared to the viscous relaxationtime a^2/ν (ν: dynamic viscosity of the fluid; a: radius of the suspended spheres). For e.g. spheres of 0.5μ radius in water at room temperature, this relaxation time is $2.5\cdot10^{-7}$s and may be neglected in many (experimental) situations.

$$\vec{u}_i = - \sum_{j=1}^{N} \underline{\mu}_{ij} \cdot \vec{K}_j . \tag{3}$$

(We have assumed here that the fluid exerts no torque on the spheres, i.e. each sphere can rotate freely; furthermore, the unperturbed fluid is assumed to be at rest.) The dependence of $\underline{\mu}_{ij}$ on the positions of the N spheres reflects their hydrodynamic interactions; in particular, a term which depends on the positions of s spheres is said to result from an s-sphere hydrodynamic interaction.

For the case of two spheres, expressions for the mobility tensors have been obtained both from an exact solution of eqs. (1)-(2)[4], as in the form of a series expansion in inverse powers of the separation R of the spheres, carried out to order R^{-7} by Kynch[5] and Felderhof[6]. These latter two calculations made use of the socalled method of reflections[3], introduced by Smoluchowski[7]. In principle, this method is not limited to the case of two spheres and indeed it was applied succesfully by Kynch[5] to obtain the dominant three- and four-sphere contributions to the mobilities. However, because of the complexity of the reflection method no general expression could be given, with which one could compute the mobilities for an arbitary number of spheres to the accuracy desired. Such expressions were finally obtained by Mazur and van Saarloos[8], by the socalled method of induced forces[9,10]. With this alternative method it is possible to reduce the problem to that of solving a hierarchy of linear algebraic equations, which proves to be very efficient in studying more than two spheres. (A similar approach to many-sphere hydrodynamic interactions has been taken by Yoshizaki and Yamakawa[11].) In this way, Mazur and van Saarloos[8] obtained the mobility tensors in the form of a power series in R^{-1}, where R is a typical distance between spheres. It was found, in particular, that the dominant contributions from clusters of s spheres $(s>2)$ are of order R^{5-3s}. (To order R^{-7}, the two-, three- and four-sphere contributions found by Kynch[5] were recovered.)

For a statistical theory of concentrated suspensions the formulae for hydrodynamic interactions obtained by Mazur and van Saarloos[8] will, in this thesis, prove to be most powerful because of their not being limited to a small number of spheres. Indeed, using these formulae we shall be able to "resum" (in a statistical sense) the many-body hydrodynamic interactions between an arbitrary number of spheres. This technique will be applied to study both diffusion (or Brownian motion) of the spheres and the effective viscosity of the suspension. We shall now briefly discuss these two subjects of our investigation.

3. Diffusion and light-scattering

Brownian motion of suspended particles, first studied by Einstein[12] in the beginning of this century, has become a subject of renewed interest with the emergence of spectroscopic techniques to observe this motion through correlations in the intensity of light scattered by the suspension[1c,13]. By measuring the average temporal auto-correlation of the scattered intensity - for scattering wavevector $\vec{k}$ and correlation delay time τ - one can obtain the dynamic structure factor $G(k,\tau)$,

$$G(k,\tau) \equiv N^{-1} \sum_{i,j=1}^{N} \langle\langle e^{i\vec{k}\cdot[\vec{R}_j(\tau)-\vec{R}_i(0)]} \rangle\rangle. \tag{4}$$

This function (which depends on the magnitude k of the wavevector only) *is the spatial Fourier transform of the particle number density* auto-correlation function. (The brackets $\langle\langle\ldots\rangle\rangle$ in eq. (4) denote an average over an equilibrium ensemble of suspensions.)

For the time derivative of eq. (4) we can write (using stationarity of the ensemble)

$$\frac{\partial}{\partial\tau} G(k,\tau) = -N^{-1} \sum_{i,j} \int_0^{\tau} dt \, \langle\langle \vec{k}\cdot\vec{u}_i(0)\vec{u}_j(t)\cdot\vec{k} \, e^{i\vec{k}\cdot[\vec{R}_j(t)-\vec{R}_i(0)]} \rangle\rangle. \tag{5}$$

As argued by Pusey and Tough[14] (on the basis of Langevin equations for the dynamics of the particles) the decay of the structure factor determined by this equation is described by a different diffusion coefficient for "short" and "long" times - relative to the structural relaxation time τ_C in which the configuration of the particles changes appreciably due to Brownian motion. On the short time scale $\tau \ll \tau_C$, eq. (5) simplifies to[14]

$$\frac{\partial}{\partial\tau} G(k,\tau) = -k^2 D(k) G(k,0), \tag{6}$$

with the diffusion coefficient D(k) given by

$$D(k) \equiv k_B T [Nk^2 G(k,0)]^{-1} \sum_{i,j=1}^{N} \langle \vec{k}\cdot\underline{\mu}_{ij}\cdot\vec{k}\, e^{i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)} \rangle. \tag{7}$$

Here $\langle\ldots\rangle$ denotes an equilibrium average over the positions of the spheres and k_B and T denote Boltzmann's constant and the temperature respectively. We remark that in the derivation of eq. (6) from eq. (5) it has also been assumed that τ is much larger than the correlation time $\tau_B = m(6\pi\eta a)^{-1}$ of the fluctuating velocities of the particles (with mass m). Use has in fact been made of the relation

$$\langle\langle \int_0^\tau dt\ \vec{u}_i(0)\vec{u}_j(t) \rangle\rangle_{\vec{R}^N} = k_B T\ \underline{\mu}_{ij}, \tag{8}$$

which holds for $\tau_B \ll \tau \ll \tau_C$. Here the brackets denote an average over the velocities of the spheres only, for given positionvectors $\vec{R}^N$.

For the systems studied in this thesis the time $\tau_C \gtrsim 10^{-2}$s is indeed very much larger than τ_B, which is of the order of 10^{-8}s. There is therefore a large "plateau" time scale $\tau_B \ll \tau \ll \tau_C$ on which the regression law (6)-(7) should hold. In our analysis we shall restrict ourselves to this time scale, which forms the most simple regime. To determine the decay of the structure factor for long times $\tau \gg \tau_C$, on the other hand, turns out to be a much more difficult problem - even without considering any hydrodynamic interactions[15]. We remark that in a light-scattering experiment both the short and long time scales in the diffusion regime are accesible.

To conclude our discussion of diffusion we mention that the short-time decay of the *self*-dynamic structure factor

$$G_s(k,\tau) \equiv N^{-1} \sum_{i=1}^{N} \langle\langle e^{i\vec{k}\cdot[\vec{R}_i(\tau)-\vec{R}_i(0)]} \rangle\rangle \tag{9}$$

is described (as in eq. (6)) by the k-independent self-diffusion coefficient D_s,

$$D_s \equiv k_B T N^{-1} \sum_{i=1}^{N} < \frac{1}{3} \operatorname{Tr} \underset{=}{\mu}_{ii} >. \qquad (10)$$

(Tr denotes the trace of a tensor.) From a comparison with eq. (7) it follows that

$$D_s = \lim_{k \to \infty} D(k), \qquad (11)$$

and D_s can therefore be measured in a light-scattering experiment at large scattering vectors[16]. (For an alternative technique using "tracer" particles with a different refractive index, see ref. 17.)

4. Effective viscosity

On a length scale much larger than the dimensions of the suspended particles a suspension behaves on average as a fluid with an "effective" viscosity η^{eff} which differs from the viscosity η of the solvent due to perturbations of the flow by the presence of the spheres. The first to study the effective viscosity was again Einstein[18] in 1906 and this quantity has played a central role in the rheology of suspensions ever since[1a,3]. One can determine the effective viscosity by calculating the average perturbations to a sufficiently slowly varying shearing field of flow imposed by an external force. In this thesis we shall neglect pertubations arising from Brownian motion of the spheres, which may give a non-vanishing contribution after averaging because of deviations of the distribution function of the positions of the spheres from its equilibrium form[19]. For this reason the validity of our analysis is again (as in the case of diffusion discussed above) limited to a time scale short compared to the structural relaxation time τ_C, since on this time scale perturbations of the distribution function may be neglected. Concerning the long-time ($\tau >> \tau_C$) regime, results have as yet only been obtained for dilute systems[19], where it has been shown that contributions from Brownian motion give an increase of the effective viscosity.

Unfortunately, little is known experimentally about time-dependent effects in the rheology of suspensions. For an understanding of the influence of Brownian motion, dynamic measurements of the effective viscosity would be of great value.

5. Outline of the contents of chapters II to IV

In chapters III and IV we present a theory for the concentration dependence of respectively diffusion coefficient and effective viscosity of a suspension of spherical particles. The method by which these quantities are calculated is introduced in its most simple form in chapter II, for the case of self-diffusion. The main contents of these three chapters are the following.

As a preliminary, we demonstrate in ch. II that the assumption of pairwise additivity of hydrodynamic interactions is unjustified if the suspension is not dilute, by extending the density expansion of the self-diffusion coefficient D_s to second order. A theory which is not restricted to the dilute regime will therefore have to account for many-body hydrodynamic interactions between an arbitrary number of spheres. The expansion of D_s in density-fluctuation correlation functions of increasing order described in ch. II satisfies this requirement. The zeroth order term in this socalled fluctuation expansion contains the resummed contributions from interactions of 2,3,4,5,... spheres - in the absence of correlations. Higher order terms contain corrections to this result from correlations between fluctuations in the concentration of the spheres. As we shall see in ch. II, these corrections are important, especially at the highest concentrations considered.

For this reason we examine, in ch. III, also an alternative expansion in correlation functions, which is obtained from the previous one by a partial resummation of higher order correlations. In this second fluctuation expansion contributions from an important class of self-correlations (these are correlations which would also be present in the hypothetical case of penetrable spheres) are included already in the zeroth order term. Both the comparison with experiments and the calculation of the lowest order correction indicate that this zeroth order term gives reliable results for the diffusion coefficient over the whole concentration range. We conclude the third chapter with an interpretation of the lowest order term in the fluctuation expansion of D(k) (defined in eq. (7)) in terms of an *effective* pair-mobility, which reflects the fact that in an averaged sense a pair of spheres interacts hydrodynamically via the *suspension* - rather than through the pure fluid.

In ch. IV the same expansion technique used in the previous chapter for the case of diffusion, is applied to study the effective viscosity. As we shall see, outside the dilute regime it is essential to take the finite particle size into account and the point-particle approximation in particular breaks down completely for a sufficiently concentrated suspension. This thesis concludes in ch. IV with a comparison of the results obtained for diffusion and viscosity. It is shown that the effective pair-mobility introduced in the previous chapter in the context of diffusion contains the effective viscosity of the suspension. This serves to support the experimental observation (first made by Cebula et al.^{20}) that the product of self-diffusion coefficient and effective viscosity is approximately independent of the concentration.

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CHAPTER II

SELFDIFFUSION:
VIRIAL EXPANSION AND RESUMMATION OF HYDRODYNAMIC INTERACTIONS

1. Introduction

In this chapter we commence the study of transport properties of suspensions by analyzing the concentration dependence of the "short-time" self-diffusion coefficient of (uncharged) suspended spheres. This quantity (which we denote by D_s) describes diffusion of a single "tracer" particle on a time scale over which the spatial configuration of the particles is essentially constant[1,2]. If the mobilities of the spheres are known - as a function of their positions - it is possible to calculate D_s by means of a generalized Einstein relation[3], which relates D_s to an average of these mobilities over all the configurations of the spheres. Experimentally, the short-time self-diffusion coefficient can be determined from dynamic light-scattering studies: the initial decay of the temporal auto-correlation function of the scattered field at large values of the scattering vector yields values for D_s[4].

If the suspension is sufficiently dilute we can assume the hydrodynamic couplings to be pairwise additive, i.e. we need to consider only two-body hydrodynamic interactions. Most theoretical treatments of properties of suspensions are restricted to this low-density regime[*]: the linear density corrections to the values at infinite dilution of

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[*] An exception is formed by Muthukumar and coworkers who included many-body hydrodynamic interactions in their analysis of flow through porous media (cf. ref. 5 and the references therein).

D_s and of the bulk-diffusion coefficient were calculated by Batchelor[3] and by Felderhof[6] and Jones[7]. Batchelor used generalized Einstein relations for these coefficients, while Felderhof and Jones based their analysis on a Fokker-Planck equation in the many-particle coordinate space. Their results were equivalent. For the case of bulk-diffusion the value of this first order correction has been confirmed by experiments[8].

Using expressions for the mobilities in clusters of three spheres[9,10], we shall in this chapter extend (for the case of self-diffusion) the analysis of Batchelor[3] to include second order density corrections (for a related calculation see also ref. 11). As we shall see, it follows from our results that three-body hydrodynamic interactions may not be neglected if the suspension is not dilute. At still higher densities one will have to take fully into account the many-body hydrodynamic interactions. Moreover, an expansion in the density (a "virial expansion") is not appropriate in this high-density regime. For this reason we consider also an alternative expansion of the self-diffusion coefficient, in correlation functions of density fluctuations of increasing order (a "fluctuation expansion"). Each term in this expansion contains the resummed contributions from many-body hydrodynamic interactions between an *arbitrary* number of spheres. Formally, such an expansion is related to a theory of the dielectric constant of nonpolar fluids developed by Bedeaux and Mazur[12]. In that context the zeroth order term in the fluctuation expansion represents the Clausius-Mossotti formula for the dielectric constant.

In section 2 we summarize the general expressions for many-sphere mobilities obtained by Mazur and van Saarloos[10] and derive a few formulae for later use. The short-time self-diffusion coefficient D_s is expressed in terms of these mobilities in section 3. In this section we also explain a compact operator notation, which shall prove its use in this and the following chapters. In section 4 we evaluate the virial expansion of D_s to second order in the density. The alternative fluctuation expansion is carried out in sections 5,6 and 7. We shall evaluate the zeroth order term (no correlations) as well as the lowest order correction thereto, which is due to two-point correlations. The results obtained are discussed and compared with experiments in section 8.

2. Mobilities

Consider N equal-sized spherical particles with radius a and position vectors $\vec{R}_i$ (i = 1,2,...N), moving in an incompressible fluid with viscosity η, which is otherwise at rest. We describe the motion of the fluid by the linear quasi-static Stokes equation, supplemented by stick boundary conditions at the surfaces of the spheres. The velocity $\vec{u}_i$ of sphere i can be expressed as a linear combination of the forces $\vec{K}_j$, exerted by the fluid on each of the spheres j

$$\vec{u}_i = - \sum_{j=1}^{N} \underline{\mu}_{ij} \cdot \vec{K}_j \ , \ i = 1,2,...N. \tag{2.1}$$

The mobility tensors $\underline{\mu}_{ij}$ depend on the configuration of the N spheres; a term in $\underline{\mu}_{ij}$ which depends on the positions of s spheres is said to reflect s-body hydrodynamic interactions. In eq. (2.1) we have assumed that the fluid exerts no torque on the spheres, i.e. each sphere can rotate freely.

The general expression for the mobilities, as derived in ref. 10, has the structure of an infinite series of reflections or scatterings from the spheres,

$$6\pi\eta a \underline{\mu}_{ij} = \underline{1}\delta_{ij} + \underline{A}_{ij}^{(1,1)} + \sum_{s=1}^{\infty} \sum_{m_1=2}^{\infty} \sum_{m_2=2}^{\infty} \cdots \sum_{m_s=2}^{\infty} \sum_{\substack{j_1=1 \\ j_1 \neq i}}^{N} \sum_{\substack{j_2=1 \\ j_2 \neq j_1}}^{N} \cdots \sum_{\substack{j_s=1 \\ j_s \neq j_{s-1}, j}}^{N}$$

$$\underline{A}_{ij_1}^{(1,m_1)} \odot \underline{B}^{(m_1,m_1)^{-1}} \odot \underline{A}_{j_1 j_2}^{(m_1,m_2)} \odot \cdots \underline{B}^{(m_s,m_s)^{-1}} \odot \underline{A}_{j_s j}^{(m_s,1)} \ , \tag{2.2}$$

and is given as a sum of products of tensors called connectors. The connector $\underline{A}_{ij}^{(n,m)}$ ($i \neq j$) is a tensor of rank n + m, which characterizes a hydrodynamic interaction between a force multipole of order n on sphere i and a multipole of order m on sphere j. This connector is a function of $\vec{R}_{ij} \equiv \vec{R}_j - \vec{R}_i$ of order $(a/|\vec{R}_{ij}|)^{n+m-1}$ and hence, for large separation of the spheres, low values of n and m dominate. By definition these connectors are zero for i = j. The tensor $\underline{B}^{(m,m)^{-1}}$ is a generalized inverse of a tensor $\underline{B}^{(m,m)}$ of rank 2m which does not depend on the positions of the spheres. The notation $\underline{A}_{ij}^{(n,m)} \odot \underline{B}^{(m,m)^{-1}}$ prescribes an m-fold contraction, with the convention that the last index of the first tensor is contracted with the first index of the second tensor, etc.

The general expressions for the connectors are (cf. ref. 10)

$$\underline{A}_{ii}^{(n,m)} = 0, \qquad (2.3)$$

$$\underline{A}_{ij}^{(n,m)} = \int d\vec{r} \int d\vec{r}\,'\ \delta(\vec{R}_i - \vec{r})\delta(\vec{R}_j - \vec{r}\,')\ \underline{A}^{(n,m)}(\vec{r}\,' - \vec{r}),\ i \neq j, \qquad (2.4)$$

with the connector field $\underline{A}^{(n,m)}(\vec{r})$ given by

$$\underline{A}^{(n,m)}(\vec{r}) = 6\pi a^3\ (2n-1)!!(2m-1)!!\ i^{m-n}(2\pi)^{-3} \int d\vec{k}\ e^{-i\vec{k}\cdot\vec{r}}\ (ak)^{-2}$$

$$\times \left(\overline{\frac{\partial^{n-1}}{\partial(a\vec{k})^{n-1}}}\ \frac{\sin(ak)}{ak} \right) (\underline{1} - \hat{k}\hat{k}) \left(\overline{\frac{\partial^{m-1}}{\partial(a\vec{k})^{m-1}}}\ \frac{\sin(ak)}{ak} \right). \qquad (2.5)$$

The tensor $\underline{B}^{(2,2)^{-1}}$ is given by*

$$\underline{B}^{(2,2)^{-1}} = -\frac{10}{9}\underline{\Delta}^{(2,2)}. \qquad (2.6)$$

The tensor $\underline{B}^{(m,m)}$ for m>3 is defined, in terms of the connector field (2.5), by

$$\underline{B}^{(m,m)} = -\underline{A}^{(m,m)}(\vec{r} = 0),\ m > 3. \qquad (2.7)$$

The inverse of this tensor is evaluated explicitly below.

In the above equations (2n-1)!! ≡ 1·3·5·...·(2n-3)·(2n-1), $k \equiv |\vec{k}|$,

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*The tensor $\underline{B}^{(2,2)^{-1}}$ defined here corresponds to $\underline{B}^{(2s,2s)^{-1}}$ in ref. 10.

$\hat{k} \equiv \vec{k}/k$. The notation $\overline{\vec{b}^{\,p}}$ denotes an irreducible tensor of rank p, i.e. a tensor traceless and symmetric in any pair of its indices, constructed from a p-fold ordered product of the vector $\vec{b}$ (in the present context $\vec{b}$ stands for $\partial/\partial(a\vec{k})$). For p = 1,2,3 one has (see e.g. ref. 14)

$$\overline{b_\alpha} = b_\alpha \;, \quad \overline{b_\alpha b_\beta} = b_\alpha b_\beta - \frac{1}{3}\,\delta_{\alpha\beta} b^2 \;,$$

$$\overline{b_\alpha b_\beta b_\gamma} = b_\alpha b_\beta b_\gamma - \frac{1}{5}\,(\delta_{\alpha\beta} b_\gamma + \delta_{\alpha\gamma} b_\beta + \delta_{\beta\gamma} b_\alpha) b^2 \;. \tag{2.8}$$

The tensor $\underline{\Delta}^{(2,2)}$ used in eq. (2.6) belongs to a class of tensors $\underline{\Delta}^{(n,n)}$ of rank 2n which project out the irreducible part of a tensor of rank n:

$$\underline{\Delta}^{(n,n)} \odot \vec{b}^{\,n} = \vec{b}^{\,n} \odot \underline{\Delta}^{(n,n)} = \overline{\vec{b}^{\,n}} \;. \tag{2.9}$$

For n = 1,2 we have[14]

$$\Delta^{(1,1)}_{\alpha\beta} = \{\underline{1}\}_{\alpha\beta} = \delta_{\alpha\beta} \;,$$

$$\Delta^{(2,2)}_{\alpha\beta\gamma\delta} = \frac{1}{2}\,\delta_{\alpha\delta}\delta_{\beta\gamma} + \frac{1}{2}\,\delta_{\alpha\gamma}\delta_{\beta\delta} - \frac{1}{3}\,\delta_{\alpha\beta}\delta_{\gamma\delta} \;. \tag{2.10}$$

The general expression for the mobilities as a function of the positions of the spheres (2.2) constitutes an expansion in the inverse interparticle distance 1/R. An explicit evaluation up to and including terms of order $(1/R)^7$ can be found in ref. 10.

Equations (2.3)-(2.10) define in principle all the quantities appearing in expression (2.2) for the mobilities. For later use it is convenient to rewrite the connector field (2.5) (from which connectors are formed according to eqs. (2.4) and (2.7)) in a somewhat different form, using the identity

$$\overline{\frac{\partial^p}{\partial \vec{k}^p}}\,\frac{\sin k}{k} = \overline{\hat{k}^{\,p}}\,(-1)^p \left(\frac{\pi}{2k}\right)^{\frac{1}{2}} J_{p+\frac{1}{2}}(k) \;, \quad p = 0,1,2,\ldots \;, \tag{2.11}$$

where $J_{p+\frac{1}{2}}$ is the Besselfunction of order $p+\frac{1}{2}$. Eq. (2.11) follows from the definition[15]

$$J_{p+\frac{1}{2}}(k) = (-1)^p \left(\frac{2k}{\pi}\right)^{\frac{1}{2}} k^p \, (k^{-1} d/dk)^p \, \frac{\sin k}{k} \tag{2.12}$$

and the relation[16]

$$\frac{\overline{\partial^p}}{\partial \vec{k}^p} f(k) = \overline{\vec{k}^p} \, (k^{-1} d/dk)^p \, f(k) \; . \tag{2.13}$$

If we now define a Fourier-transformed connector field

$$\underline{A}^{(n,m)}(\vec{k}) = \int d\vec{r} \, e^{i\vec{k}\cdot\vec{r}} \, \underline{A}^{(n,m)}(\vec{r}) \quad , \tag{2.14}$$

we have, in view of eqs. (2.5) and (2.11),

$$\begin{aligned} \underline{A}^{(n,m)}(\vec{k}) &= 6\pi a^3 \, (2n-1)!!(2m-1)!! \; i^{n-m} \, \frac{\pi}{2} \, (ak)^{-3} \\ &\times \; J_{n-\frac{1}{2}}(ak) J_{m-\frac{1}{2}}(ak) \; \overline{\hat{k}^{n-1}} \; (\underline{1} - \hat{k}\hat{k}) \; \overline{\hat{k}^{m-1}} \quad . \end{aligned} \tag{2.15}$$

The above relation may be used to evaluate the tensor $\underline{B}^{(m,m)}$ explicitly for $m \geqslant 3$, since (cf. eq. (2.7))

$$\underline{B}^{(m,m)} = -(2\pi)^{-3} \int_0^\infty k^2 dk \int d\hat{k} \; \underline{A}^{(m,m)}(\vec{k}) \quad , \qquad m \geqslant 3 \; . \tag{2.16}$$

The scalar part of the above integration may be evaluated with help of the formula (ref. 15, pg. 679)

$$\int_0^\infty dk \; k^{-1} J^2_{m-\frac{1}{2}}(k) = (2m-1)^{-1} \; . \tag{2.17}$$

Using, for the angular integration in eq. (2.16), the results given in appendix A (see eq. (A.9)), we find the explicit expression

$$\begin{aligned} \underline{B}^{(m,m)} = &- \frac{3}{2} \, (m-1)!(2m-3)!! \Big(\underline{\Delta}^{(m-1,\mathrm{id},m-1)} - \frac{m}{2m+1} \, \underline{\Delta}^{(m,m)} \\ &- \frac{m-1}{2m-1} \, \underline{\Delta}^{(m-1,m-1)} \odot^{m-2} \underline{\Delta}^{(m-1,m-1)} \Big) \quad , \qquad m \geqslant 3, \end{aligned} \tag{2.18}$$

where the symbol $\odot^{\ell}$ denotes an ℓ-fold contraction. The tensor $\underline{\Delta}^{(m-1,id,m-1)}$ is a tensor of rank 2m with elements

$$\Delta^{(m-1,id,m-1)}_{\alpha_1\cdots\alpha_{m-1},\beta\gamma,\delta_1\cdots\delta_{m-1}} = \delta_{\beta\gamma}\ \Delta^{(m-1,m-1)}_{\alpha_1\cdots\alpha_{m-1},\delta_1\cdots\delta_{m-1}} \ . \tag{2.19}$$

This tensor acts as a unit tensor when contracted with a tensor $\underline{T}^{(m)}$ of rank m which is irreducible (traceless and symmetric) in its first m-1 indices

$$\underline{\Delta}^{(m-1,id,m-1)} \odot \underline{T}^{(m)} = \underline{T}^{(m)}. \tag{2.20}$$

The tensor $\underline{B}^{(m,m)^{-1}}$ appearing in eq. (2.2) is the generalized inverse of $\underline{B}^{(m,m)}$ in the space of tensors of rank m which are irreducible in their first m-1 indices. It is therefore determined by the equation

$$\underline{B}^{(m,m)^{-1}} \odot \underline{B}^{(m,m)} = \underline{\Delta}^{(m-1,id,m-1)} \ , \quad m\geq 3. \tag{2.21}$$

The result

$$\underline{B}^{(m,m)^{-1}} = -\left[\frac{3}{2}(m-1)!(2m-3)!!\right]^{-1}\Big[\underline{\Delta}^{(m-1,id,m-1)} + \frac{m}{m+1}\,\underline{\Delta}^{(m,m)}$$
$$+\left(\frac{m-1}{m-2}\right)\left(\frac{2m-3}{2m-1}\right)\underline{\Delta}^{(m-1,m-1)} \odot^{m-2} \underline{\Delta}^{(m-1,m-1)}\Big] \ , \quad m\geq 3, \tag{2.22}$$

may - with help of formulae (A.3)-(A.5) in appendix A - be checked by substitution into eq. (2.21). We recall that $\underline{B}^{(2,2)^{-1}}$ is defined in eq. (2.6).

3. Self-diffusion

The short-time self-diffusion coefficient $\underline{D}_s$ is related to the mobilities discussed in section 2 by a generalized Einstein relation[3]

$$\underline{D}_s = k_B T\,\frac{1}{N}\left\langle \sum_{i=1}^{N} \underline{\mu}_{ii} \right\rangle , \tag{3.1}$$

where <...> denotes an average over all configurations of the N spheres inside a volume V. We denote the temperature and Boltzmann's constant by T and k_B, respectively. The short-time self-diffusion coefficient $\underline{D}_s$ describes the diffusion of a single "tracer" particle, over distances small compared to the interparticle separation (see in this connection the discussion in ref. 2). Combining eqs. (2.2) and (3.1) we obtain (see also eq. (2.3))

$$\underline{D}_s/D_o = \underline{1} + N^{-1}\langle \sum_{s=1}^{\infty}\sum_{m_1=2}^{\infty}\cdots\sum_{m_s=2}^{\infty}\sum_{\substack{i=1\\ i\neq j_s}}^{N}\sum_{\substack{j_1=1\\ j_1\neq i}}^{N}\cdots\sum_{\substack{j_s=1\\ j_s\neq j_{s-1}}}^{N}\underline{A}^{(1,m_1)}_{ij_1}\odot\underline{B}^{(m_1,m_1)^{-1}}\odot\underline{A}^{(m_1,m_2)}_{j_1j_2}\odot\cdots\underline{B}^{(m_s,m_s)^{-1}}\odot\underline{A}^{(m_s,1)}_{j_si}\rangle\,, \qquad (3.2)$$

where we have defined

$$D_o = k_BT\,(6\pi\eta a)^{-1}\,. \qquad (3.3)$$

Thus for isolated spherical particles $\underline{D}_s = D_o\,\underline{1}$, the familiar Stokes-Einstein result.

Equation (3.2) will be the starting point for the virial expansion of $\underline{D}_s$, evaluated up to second order in section 4. In order to study also the behaviour of $\underline{D}_s$ at higher densities, we shall cast this equation in a different form, which permits a formal resummation. We first redefine the connector field in the following way

$$\underline{\tilde{A}}^{(n,m)}(\vec{r}) = \underline{A}^{(n,m)}(\vec{r}) \text{ if } \vec{r}\neq 0\,,\quad \underline{\tilde{A}}^{(n,m)}(\vec{r}=0)=0. \qquad (3.4)$$

If we now use definition (2.4), eq. (3.2) becomes

$$\underline{D}_s/D_o = \underline{1} + N^{-1}\sum_{s=1}^{\infty}\sum_{m_1=2}^{\infty}..\sum_{m_s=2}^{\infty}\int d\vec{r}_0\int d\vec{r}_1..\int d\vec{r}_s\langle\sum_{i=1}^{N}\delta(\vec{R}_i-\vec{r}_0)\sum_{j_1=1}^{N}\delta(\vec{R}_{j_1}-\vec{r}_1)\;..\sum_{j_s=1}^{N}\delta(\vec{R}_{j_s}-\vec{r}_s)\,\underline{\tilde{A}}^{(1,m_1)}(\vec{r}_1-\vec{r}_0)\odot\underline{B}^{(m_1,m_1)^{-1}}\odot..\,\underline{\tilde{A}}^{(m_s,1)}(\vec{r}_0-\vec{r}_s)\rangle. \qquad (3.5)$$

Note that the introduction of the modified connector field $\tilde{\underline{A}}^{(n,m)}(\vec{r})$ enabled us to perform the summations over the particle indices without restriction. Due to homogeneity of the suspension, the integrand in eq. (3.5) is invariant under a translation of the particle position vectors over $\vec{r}_0$. After a change of integration variables eq. (3.5) takes the form

$$\underline{D}_s/D_o = \underline{1} + n_o^{-1} \sum_{s=1}^{\infty} \sum_{m_1=2}^{\infty} .. \sum_{m_s=2}^{\infty} \int d\vec{r}_1 \int d\vec{r}_2 .. \int d\vec{r}_s \langle n(\vec{r} = 0)\, \tilde{\underline{A}}^{(1,m_1)}(\vec{r}_1) n(\vec{r}_1)$$

$$\odot\, \underline{B}^{(m_1,m_1)^{-1}} \odot \tilde{\underline{A}}^{(m_1,m_2)}(\vec{r}_2 - \vec{r}_1)\, n(\vec{r}_2) \odot .. \underline{B}^{(m_s,m_s)^{-1}} \odot \tilde{\underline{A}}^{(m_s,1)}(-\vec{r}_s) \rangle, \quad (3.6)$$

where the microscopic density field, with average $n_o = N/V$, is given by

$$n(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{R}_i - \vec{r}) \; . \quad (3.7)$$

Equation (3.6) may alternatively be written in operator notation

$$\underline{D}_s/D_o = \underline{1} + n_o^{-1} \sum_{s=1}^{\infty} \sum_{m_1=2}^{\infty} \ldots \sum_{m_s=2}^{\infty} \langle \{ n\, \tilde{\underline{A}}^{(1,m_1)} n \odot \underline{B}^{(m_1,m_1)^{-1}} \odot \tilde{\underline{A}}^{(m_1,m_2)} n$$

$$\ldots \odot \underline{B}^{(m_s,m_s)^{-1}} \odot \tilde{\underline{A}}^{(m_s,1)} \}(0|0) \rangle, \quad (3.8)$$

where n and $\tilde{\underline{A}}^{(n,m)}$ (written without argument) are linear integral operators with kernels

$$n(\vec{r}|\vec{r}') = n(\vec{r})\, \delta(\vec{r}' - \vec{r}) \; , \quad (3.9)$$

$$\tilde{\underline{A}}^{(n,m)}(\vec{r}|\vec{r}') = \tilde{\underline{A}}^{(n,m)}(\vec{r}' - \vec{r}). \quad (3.10)$$

We see that in $\vec{r}$-representation n is a diagonal operator and $\tilde{\underline{A}}^{(n,m)}$ a convolution operator. The notation $\{\ldots\}(0|0)$ prescribes an evaluation of the kernel of the operator between curly brackets at $\vec{r} = \vec{r}' = 0$.

Next we define matrices $\mathcal{A}$ and $\mathcal{B}^{-1}$ with elements

$$\{\mathcal{A}\}_{n,m} = \underline{\tilde{A}}^{(n,m)} , \tag{3.11}$$

$$\{\mathcal{B}^{-1}\}_{n,m} = \delta_{nm}\, \underline{B}^{(m,m)^{-1}} , \tag{3.12}$$

and projection operators $\mathcal{P}$ and $\mathcal{Q} = \mathcal{1} - \mathcal{P}$

$$\{\mathcal{P}\}_{n,m} = \delta_{n1}\delta_{m1} , \quad \{\mathcal{Q}\}_{n,m} = \delta_{nm} - \delta_{n1}\delta_{m1} . \tag{3.13}$$

With these notations we may write e.g.*

$$\sum_{m=2}^{\infty} \underline{\tilde{A}}^{(1,m)} \odot \underline{B}^{(m,m)^{-1}} \odot \underline{\tilde{A}}^{(m,1)} = \mathcal{P}\mathcal{A}\mathcal{Q}\mathcal{B}^{-1}\mathcal{A}\mathcal{P} \tag{3.14}$$

and eq. (3.8) takes the form

$$\underline{D}_s/D_o = \underline{1} + n_o^{-1} \sum_{s=1}^{\infty} \mathcal{P} <\{n\mathcal{A}\ (n\ \mathcal{Q}\ \mathcal{B}^{-1}\mathcal{A}\ )^s\}(0|0)> \mathcal{P} . \tag{3.15}$$

This equation can formally be resummed to yield

$$\underline{D}_s/D_o = \underline{1} + n_o^{-1}\ \mathcal{P} <\{n\mathcal{A}\ (\mathcal{1} - n\ \mathcal{Q}\mathcal{B}^{-1}\mathcal{A}\ )^{-1}\}(0|0)> \mathcal{P} , \tag{3.16}$$

where we have used the fact that, in view of definition (3.4),

$$\mathcal{P} <\{n\mathcal{A}\ \}(0|0)> \mathcal{P} = n_o\, \underline{\tilde{A}}^{(1,1)}(\vec{r} = 0) = 0. \tag{3.17}$$

We remark that it is possible to derive eq. (3.16) algebraically from eqs. (5.2)-(5.5) of ref. 10, in a way which does not require a resummation. Eq. (3.16) - which contains the full hydrodynamic interaction of the N spheres - will be the starting point for the expansion of $\underline{D}_s$ in correlations of density fluctuations, performed in section 5.

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*To be more precise: the right hand side of eq. (3.14) is a matrix with the left hand side as the only non-zero element.

4. The virial expansion

For a dilute suspension it is appropriate to express the short-time self-diffusion coefficient $\underline{D}_s$ as a power series in the density n_o (a socalled virial expansion). We shall evaluate this series up to and including terms of second order in the density. Up to this order we need consider only contributions from two- and from three-body hydrodynamic interactions; these contributions are discussed separately below.

4.1 Two-sphere contributions

A restriction of $\underline{\mu}_{ii}$ to terms which depend on the positions of at most two spheres has the following expansion in powers of $1/R$[9,10,17]

$$6\pi\eta a\, \underline{\mu}_{ii}\ (\textit{two-spheres}) = \underline{1} + \sum_{k\neq i} \left(-\frac{15}{4}\right)(a/R_{ik})^4\, \hat{r}_{ik}\hat{r}_{ik} + \sum_{k\neq i} \frac{1}{16}(a/R_{ik})^6\, (105\, \hat{r}_{ik}\hat{r}_{ik} - 17\, \underline{1}) + O(a/R)^8. \tag{4.1}$$

Here the vector $\vec{R}_{ik} \equiv \vec{R}_k - \vec{R}_i$ has magnitude $R_{ik} \equiv |\vec{R}_{ik}|$ and direction $\hat{r}_{ik} \equiv \vec{R}_{ik}/R_{ik}$. Substitution of eq. (4.1) in eq. (3.2) yields for the two-sphere contributions to $\underline{D}_s$

$$\underline{D}_s/D_o\ (\textit{two-spheres}) = \underline{1} + n_o \int d\vec{R}\; g(R) \left(-\frac{15}{4}(a/R)^4\, \hat{r}\hat{r} + \frac{1}{16}(a/R)^6\, (105\, \hat{r}\hat{r} - 17\, \underline{1})\right), \tag{4.2}$$

where $g(R)$ denotes the pair distribution function for two spheres separated by R. Up to order n_o we have (see e.g. ref. 18)

$$g(R) = \begin{cases} 0 & \text{if } R < 2a\,, \\ 1 + \frac{4}{3}\pi a^3 n_o \left(8 - 3\, R/a + \frac{1}{16}(R/a)^3\right) & \text{if } 2a \leqslant R \leqslant 4a, \\ 1 & \text{if } R > 4a\,. \end{cases} \tag{4.3}$$

An elementary integration gives the required first and second order density corrections to D_o due to two-body hydrodynamic interactions

$$\underline{D}_s \; (\textit{two-spheres}) = D_o \, \underline{1} \; [\; 1 - 1.73\phi - 0.93\phi^2 + O(\phi^3) \;], \tag{4.4}$$

where ϕ is the partial volume or volume fraction of the spheres

$$\phi = \frac{4}{3}\pi a^3 \, n_o \; . \tag{4.5}$$

4.2 Three-sphere contributions

Of the three-sphere terms in the expansion of $\underline{\mu}_{ii}$ in powers of $1/R$ we have retained the dominant one (which is of order R^{-7}), evaluated in refs. 9 and 10,

$$6\pi\eta a \, \underline{\mu}_{ii} \; (\textit{three-spheres}) = \sum_{k\neq i} \; \sum_{\ell\neq i,k} - \frac{75}{16} (a/R_{ik})^2 (a/R_{k\ell})^3 (a/R_{\ell i})^2$$
$$\times \; \hat{r}_{ik}\hat{r}_{i\ell}\big((1 - 3\xi_k^{\,2})(1 - 3\xi_\ell^{\,2}) + 6\xi_k^{\,2}\xi_\ell^{\,2} + 6\xi_i\xi_k\xi_\ell\big) + O(a/R)^9, \tag{4.6}$$

where $\xi_i \equiv \hat{r}_{ik}\cdot\hat{r}_{i\ell}$, $\xi_k \equiv \hat{r}_{ki}\cdot\hat{r}_{k\ell}$ and $\xi_\ell \equiv \hat{r}_{\ell i}\cdot\hat{r}_{\ell k}$ are direction cosines. The three-sphere contribution to $\underline{D}_s$ is obtained by averaging eq. (4.6) with the three-sphere distribution function $g(R_{12},R_{13},R_{23})$, given in lowest order by

$$g(R_{12},R_{13},R_{23}) = \begin{cases} 0 & \text{if } R_{12} < 2a \text{ or } R_{13} < 2a \text{ or } R_{23} < 2a \;, \\ 1 & \text{elsewise} \; . \end{cases} \tag{4.7}$$

After three trivial angular integrations, we are left with a three-dimensional integral over a complicated domain, determined by eq. (4.7). This integral was evaluated numerically using Monte-Carlo techniques*. The resulting three-sphere contribution to $\underline{D}_s$ is

$$\underline{D}_s \; (\textit{three-spheres}) = D_o \, \underline{1} \; [\; 1.80\phi^2 + O(\phi^3) \;]. \tag{4.8}$$

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*Use was made of the adaptive Monte-Carlo integration program RIWIAD[20].

If we add eqs. (4.4) and (4.8) we obtain the virial expansion of $\underline{D}_s$ up to second order in the density

$$\underline{D}_s\ (\textit{two- and three-spheres}) = D_o\,\underline{1}[1 - 1.73\phi + 0.88\phi^2 + O(\phi^3)]. \quad (4.9)$$

The term of order ϕ is well known[3,7]. Batchelor[3] used *exact* expressions for the two-sphere mobility tensors and found -1.83ϕ for the correction of order ϕ. Comparison with eq. (4.9) shows that the terms of order R^{-8} and higher neglected in eq. (4.1) are not very important. Concerning the three-sphere contributions neglected in eq. (4.6) (of order R^{-9} and higher) we can say the following: a calculation of the contribution to $\underline{D}_s$ due to a typical three-sphere mobility term of order R^{-9} was found to give about 1% of the value in eq. (4.8)*, which results from the only term of order R^{-7}.

We defer a discussion of our result (4.9) to section 8.

5. The fluctuation expansion

The fluctuations in the microscopic density field are defined by

$$n(\vec{r}) = n_o + \delta n(\vec{r}). \quad (5.1)$$

The average $\langle\delta n(\vec{r})\rangle$ equals zero by definition, while[20]

$$\langle\delta n(\vec{r})\delta n(\vec{r}\,')\rangle = n_o\delta(\vec{r}\,' - \vec{r}) + n_o^2[g(|\vec{r}\,' - \vec{r}|) - 1], \quad (5.2)$$

with g(r) the pair distribution function.

Our aim is to expand the expression between curly brackets in eq. (3.16) in powers of δn. This can be done most conveniently by using first the identity (A is an arbitrary operator)

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*Using the notation of ref. 10: we found that the sequence of connectors $\underline{G}^{(1,2s)}(\vec{R}_1):\underline{B}^{(2s,2s)^{-1}}:\underline{H}^{(2s,2s)}(\vec{R}_{12}):\underline{B}^{(2s,2s)^{-1}}:\underline{G}^{(2s,1)}(-\vec{R}_2)$ contributes $-0.016\phi^2$ to D_s/D_o.

$$[1 - (n_o + \delta n)A]^{-1} = (1 - n_oA)^{-1}\ [1 - \delta nA(1 - n_oA)^{-1}\ ]^{-1}. \qquad (5.3)$$

Substitution of (5.1) in eq. (3.16) gives, with the aid of (5.3), the alternative expression for $\underline{D}_s$

$$\underline{D}_s/D_o = \underline{1} + n_o^{-1}\ \mathcal{P}\langle\{n\, A_{n_o}\ [\ \mathit{1} - \delta n\ \mathcal{QB}^{-1}\ A_{n_o}\ ]^{-1}\}(0|0)\rangle\, \mathcal{P}, \qquad (5.4)$$

where the renormalized matrix of connectors A_{n_o} is defined as

$$A_{n_o} \equiv A\ \ [\mathit{1} - n_o\ \mathcal{QB}^{-1}\ A\,]^{-1}. \qquad (5.5)$$

This renormalization accounts for the fact that fluctuations in the concentration of the spheres interact hydrodynamically via the *suspension* rather than through the pure fluid.

If we expand the expression between curly brackets in eq. (5.4) in powers of δn, we obtain an expansion of $\underline{D}_s$ in correlations of density fluctuations of higher and higher order (a "fluctuation expansion")

$$\underline{D}_s = \underline{D}_s^{(0)} + \underline{D}_s^{(2)} + \ldots\ , \qquad (5.6)$$

where $\underline{D}_s^{(p)}$ contains terms of order $\langle(\delta n)^p\rangle$.

The zeroth order term $\underline{D}_s^{(0)}$ is given by

$$\underline{D}_s^{(0)}/D_o = \underline{1} + \underline{A}_{n_o}^{(1,1)}(\vec{r}{=}0), \qquad (5.7)$$

where the renormalized connector field $\underline{A}_{n_o}^{(n,m)}(\vec{r})$ is the kernel of the convolution operator $\underline{A}_{n_o}^{(n,m)}$, which in turn is an element of the matrix A_{n_o}

$$\underline{A}_{n_o}^{(n,m)} = \{\ A_{n_o}\}_{n,m}. \qquad (5.8)$$

The renormalized connector field will be evaluated in the next section; an explicit expression for $\underline{D}_s^{(0)}$ is given in section 7.

We shall include in our calculation of $\underline{D}_s$ the lowest order correction to $\underline{D}_s^{(0)}$ due to fluctuations in the concentration of the suspended particles. This correction $\underline{D}_s^{(2)}$ results from terms of order $\langle(\delta n)^2\rangle$ in eq. (5.4) and is given by

$$\underline{D}_s^{(2)}/D_o = n_o^{-1}\, \mathcal{P}\langle\{\delta n\, \mathcal{A}_{n_o}\, \delta n\, \mathcal{QB}^{-1}\, \mathcal{A}_{n_o} + n_o\, \mathcal{A}_{n_o}\, \delta n\, \mathcal{QB}^{-1}\, \mathcal{A}_{n_o}\, \delta n\, \mathcal{QB}^{-1}\, \mathcal{A}_{n_o}\}(0|0)\rangle\mathcal{P} \,, \tag{5.9}$$

or, written out explicitly,

$$\begin{aligned}
\underline{D}_s^{(2)}/D_o = {} & \sum_{m=2}^{\infty} \underline{A}_{n_o}^{(1,m)}(\vec{r}=0) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,1)}(\vec{r}=0) \\
& + \sum_{m=2}^{\infty} n_o \int d\vec{r}\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,1)}(-\vec{r})\, [g(r) - 1] \\
& + \sum_{m=2}^{\infty} \sum_{k=2}^{\infty} n_o \int d\vec{r}\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,k)}(\vec{r}=0) \odot \underline{B}^{(k,k)^{-1}} \odot \underline{A}_{n_o}^{(k,1)}(-\vec{r}) \\
& + \sum_{m=2}^{\infty} \sum_{k=2}^{\infty} n_o^2 \int d\vec{r} \int d\vec{r}\,'\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,k)}(\vec{r}\,' - \vec{r}) \odot \underline{B}^{(k,k)^{-1}} \\
& \qquad \odot \underline{A}_{n_o}^{(k,1)}(-\vec{r}\,')[g(|\vec{r}\,'-\vec{r}|)-1] .
\end{aligned} \tag{5.10}$$

Use has also been made of eq. (5.2). The contributions to $\underline{D}_s^{(2)}$ result from pair-correlations (the terms containing $g(r)-1$) and from self-correlations which would also be present in the hypothetical case of penetrable spheres.

6. Evaluation of the renormalized connectors

According to eqs. (5.5) and (5.8) the renormalized connector field $\underline{A}_{n_o}^{(n,m)}(\vec{r})$ is formally given by

$$\underline{A}_{n_o}^{(n,m)}(\vec{r}) = \underline{\tilde{A}}^{(n,m)}(\vec{r}) + \sum_{s=1}^{\infty} \sum_{m_1=2}^{\infty} \cdots \sum_{m_s=2}^{\infty} n_o^s \int d\vec{r}_1 \cdots \int d\vec{r}_s \, \underline{\tilde{A}}^{(n,m_1)}(\vec{r}_1)$$

$$\odot \, \underline{B}^{(m_1,m_1)^{-1}} \odot \underline{\tilde{A}}^{(m_1,m_2)}(\vec{r}_2 - \vec{r}_1) \odot \, .. \underline{B}^{(m_s,m_s)^{-1}} \odot \underline{\tilde{A}}^{(m_s,m)}(\vec{r} - \vec{r}_s), \quad (6.1)$$

cf. also definitions (3.10)-(3.13). We observe that we may replace $\underline{\tilde{A}}^{(n,m)}(\vec{r})$ under the integral in eq. (6.1) by $\underline{A}^{(n,m)}(\vec{r})$, since these two connector fields differ by a finite amount in a single point only, cf. eq. (3.4). Hence, in terms of the Fourier-transformed connector field defined in eq. (2.14), eq. (6.1) takes the form

$$\underline{A}_{n_o}^{(n,m)}(\vec{r}) = \underline{\tilde{A}}^{(n,m)}(\vec{r}) + \sum_{s=1}^{\infty} \sum_{m_1=2}^{\infty} \cdots \sum_{m_s=2}^{\infty} n_o^s (2\pi)^{-3} \int d\vec{k} \, e^{-i\vec{k}\cdot\vec{r}} \, \underline{A}^{(n,m_1)}(\vec{k})$$

$$\odot \, \underline{B}^{(m_1,m_1)^{-1}} \odot \underline{A}^{(m_1,m_2)}(\vec{k}) \odot \, .. \, \underline{B}^{(m_s,m_s)^{-1}} \odot \underline{A}^{(m_s,m)}(\vec{k}). \quad (6.2)$$

To proceed we make use of the formula (proven in appendix B)

$$n_o \, \underline{A}^{(n,p)}(\vec{k}) \odot \underline{B}^{(p,p)^{-1}} \odot \underline{A}^{(p,m)}(\vec{k}) = - \underline{A}^{(n,m)}(\vec{k}) \, \frac{9}{4} \pi \phi \, \varepsilon_p (2p-1)^2$$

$$\times \, (ak)^{-3} J_{p-\frac{1}{2}}^2(ak), \quad p \geqslant 2, \quad (6.3)$$

with the definition

$$\varepsilon_2 = 5/9 \ , \ \varepsilon_p = 1 \ (p \geqslant 3). \quad (6.4)$$

The volume fraction ϕ is defined in eq. (4.5). Using well known formulae for Bessel functions (cf. appendix C) we can analytically perform a summation over p in eq. (6.3)

$$\sum_{p=2}^{\infty} n_o \, \underline{A}^{(n,p)}(\vec{k}) \odot \underline{B}^{(p,p)^{-1}} \odot \underline{A}^{(p,m)}(\vec{k}) = -\phi \, S(ak) \, \underline{A}^{(n,m)}(\vec{k}), \quad (6.5)$$

where the function S(x) is given by

$$S(x) = \frac{9}{2}\,[x^{-1}\mathrm{Si}(2x) + \tfrac{1}{2}x^{-2}\cos(2x) + \tfrac{1}{4}x^{-3}\sin(2x)$$

$$- x^{-4}\sin^2 x - 4x^{-6}(\sin x - x\cos x)^2]. \qquad (6.6)$$

Here the sine-integral Si(2x) is defined by

$$\mathrm{Si}(2x) = \int_0^{2x} t^{-1}\sin t\, dt. \qquad (6.7)$$

For small values of x, S(x) behaves as

$$S(x) = 5/2 + \mathcal{O}(x^2). \qquad (6.8)$$

With the aid of formula (6.5) we can resum the formal expansion (6.2) to yield the required expression for the renormalized connector field

$$\underline{A}_{\underline{n}_0}^{(n,m)}(\vec{r}) = \underline{\tilde{A}}^{(n,m)}(\vec{r}) - (2\pi)^{-3}\int d\vec{k}\; e^{-i\vec{k}\cdot\vec{r}}\; \underline{A}^{(n,m)}(\vec{k})$$

$$\times\ \phi S(ak)[1 + \phi S(ak)]. \qquad (6.9)$$

We remark that as a consequence of the expansion (6.8), we have for r large

$$\underline{A}_{\underline{n}_0}^{(n,m)}(\vec{r}) \approx \underline{A}^{(n,m)}(\vec{r})\,(1 + \frac{5}{2}\,\phi)^{-1}. \qquad (6.10)$$

We thus see that the range of a renormalized connector is the same as the range of an unrenormalized one, or, in other words, the hydrodynamic interaction is *not screened* in the effective medium.

For the fluctuation expansion we need in particular the value $\underline{A}_{\underline{n}_0}^{(n,m)}(\vec{r}=0)$ (cf. eqs. (5.7) and (5.10)). Using, for the angular integration in eq. (6.9), the results (A.9)-(A.11) from appendix A we find

$$\underline{A}_{\underline{n}_0}^{(1,1)}(\vec{r}=0) = -\,\underline{1}\int_0^\infty dk\; k^{-1}J_{\frac{1}{2}}^{\;2}(k)\; \phi S(k)[1 + \phi S(k)]^{-1}\;, \qquad (6.11)$$

$$\underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_0}^{(m,m)}(\vec{r} = 0) \odot \underline{B}^{(m,m)^{-1}} =$$

$$= \underline{B}^{(m,m)^{-1}} (2m-1)\int_0^\infty dk\ k^{-1} J^2_{m-\frac{1}{2}}(k)\ \phi S(k)[1 + \phi S(k)]^{-1}, \qquad m \geqslant 2, \tag{6.12}$$

$$\underline{A}_{n_0}^{(m,m+2)}(\vec{r}=0) = \underline{A}_{n_0}^{(m+2,m)}(\vec{r}=0) = - \frac{3}{2}\,(m+1)!(2m-1)!!\ \underline{\Delta}^{(m+1,m+1)}$$

$$\times \int_0^\infty dk\ k^{-1} J_{m-\frac{1}{2}}(k)\ J_{m+3/2}(k)\ \phi S(k)[1 + \phi S(k)]^{-1}, \tag{6.13}$$

$$\underline{A}_{n_0}^{(n,m)}(\vec{r} = 0) = 0 \quad \text{if} \quad n \neq m \quad \text{and} \quad n \neq m \pm 2, \tag{6.14}$$

where $\underline{B}^{(m,m)^{-1}}$ ($m \geqslant 2$) is given by eqs. (2.6) and (2.22). The remaining one-dimensional integrations in the above equations may be performed numerically.

7. Numerical results for the fluctuation expansion

In section 5 we have written the fluctuation expansion of the short-time self-diffusion coefficient $\underline{D}_s$ in the form

$$\underline{D}_s = \underline{D}_s^{(0)} + \underline{D}_s^{(2)} + \ldots \ , \tag{7.1}$$

where $\underline{D}_s^{(p)}$ contains terms of order $\langle(\delta n)^p\rangle$, i.e. correlations of density fluctuations of order p.

From eqs. (5.7) and (6.11) we obtain for $\underline{D}_s^{(0)}$ the expression

$$\underline{D}_s^{(0)} = D_0\,\underline{1}\left(1 - \frac{2}{\pi}\,\phi\int_0^\infty dk\ (\sin k/k)^2\ S(k)[1 + \phi S(k)]^{-1}\right)$$

$$= D_0\,\underline{1}\,\frac{2}{\pi}\int_0^\infty dk\ (\sin k/k)^2\ [1 + \phi S(k)]^{-1}, \tag{7.2}$$

where the function S(k) is defined in eq. (6.6). A numerical

Table 1

The fluctuation expansion of D_s to second order.

ϕ	$D_s^{(0)}/D_o$	+	$D_s^{(2)}/D_o$	=	D_s/D_o
0.05	0.896	+	0.005		0.90
0.10	0.812	-	0.007		0.80
0.15	0.743	-	0.024		0.72
0.20	0.685	-	0.041		0.64
0.25	0.636	-	0.057		0.58
0.30	0.593	-	0.071		0.52
0.35	0.556	-	0.083		0.47
0.40	0.524	-	0.093		0.43
0.45	0.495	-	0.102		0.39

integration* yields the values listed in table 1.

With the aid of eqs. (6.13) and (6.14) the expression (5.10) for $\underline{D}_s^{(2)}$ reduces to

$$\begin{aligned}
\underline{D}_s^{(2)}/D_o = {} & \underline{A}_{n_o}^{(1,3)}(\vec{r} = 0) \odot \underline{B}^{(3,3)^{-1}} \odot \underline{A}_{n_o}^{(3,1)}(\vec{r} = 0) \\
& + \sum_{m=2}^{\infty} n_o \int d\vec{r}\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,m)}(\vec{r}=0) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,1)}(-\vec{r}) \\
& +2 \sum_{m=2}^{\infty} n_o \int d\vec{r}\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,m+2)}(\vec{r}=0) \odot \underline{B}^{(m+2,m+2)^{-1}} \odot \underline{A}_{n_o}^{(m+2,1)}(-\vec{r}) \\
& + \sum_{m=2}^{\infty} n_o \int d\vec{r}\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,1)}(-\vec{r})\, [g(r) - 1] \\
& + \sum_{m=2}^{\infty} \sum_{k=2}^{\infty} n_o^2 \int d\vec{r} \int d\vec{r}\,'\, \underline{A}_{n_o}^{(1,m)}(\vec{r}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{n_o}^{(m,k)}(\vec{r}\,' - \vec{r}) \odot \underline{B}^{(k,k)^{-1}} \\
& \qquad \odot \underline{A}_{n_o}^{(k,1)}(-\vec{r}\,')\, [g(|\vec{r}\,' - \vec{r}|)-1].
\end{aligned} \tag{7.3}$$

---

*We used an adaptive routine based on Gauss quadrature rules[21]. This routine, together with an algorithm for the evaluation of the sine-integral appearing in definition (6.6), is part of the NAG-library (Oxford).

We have numerically evaluated all the terms in eq. (7.3) not containing connectors $\underline{A}_{n_0}^{(n,m)}(\vec{r})$ with n or m larger than 2, i.e. restricting ourselves to corrections to $\underline{D}_s^{(0)}$ due to monopolar and dipolar hydrodynamic interactions between density fluctuations. The results can also be found in table 1. We approximated g(r) by the solution of the Percus-Yevick equation for hard spheres, as found by Wertheim and Thiele[22]. Details of the calculations are given in appendix D.

8. Discussion

We have calculated the concentration dependence of the short-time self-diffusion coefficient D_s for spherical particles in suspension. For low values of the volume fraction ϕ a virial expansion is appropriate. We found

$$\underline{D}_s = D_o \underline{1} \, [\, 1 - 1.73\phi + 0.88\phi^2 + \mathcal{O}(\phi^3) \,]. \tag{8.1}$$

Only two-body hydrodynamic interactions contribute to the - well known[3,7] - term of order ϕ, which dominates if the suspension is very dilute. However, many-body hydrodynamic interactions may not be neglected at higher densities: a neglect of three-sphere contributions would give a value of $- 0.93\phi^2$ instead of $+ 0.88\phi^2$ for the term of order ϕ^2 in eq. (8.1). In a concentrated suspension it is therefore essential to fully take into account the many-body hydrodynamic interactions between an *arbitrary* number of spheres*.

The expansion of D_s in correlations of fluctuations in the concentration of the suspended particles satisfies the above requirement. In fig. 1 we have plotted the results from this fluctuation expansion, carried out to second order. At low values of ϕ we can compare these

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*Van Megen, Snook and Pusey[23], in contrast, calculated the diffusion coefficient by averaging the two- and three-sphere mobilities given in eqs. (4.1) and (4.6) with "exact" distribution functions (as known from computer simulations). The neglect of hydrodynamic interactions between four and more particles in a concentrated suspension can however not be justified.

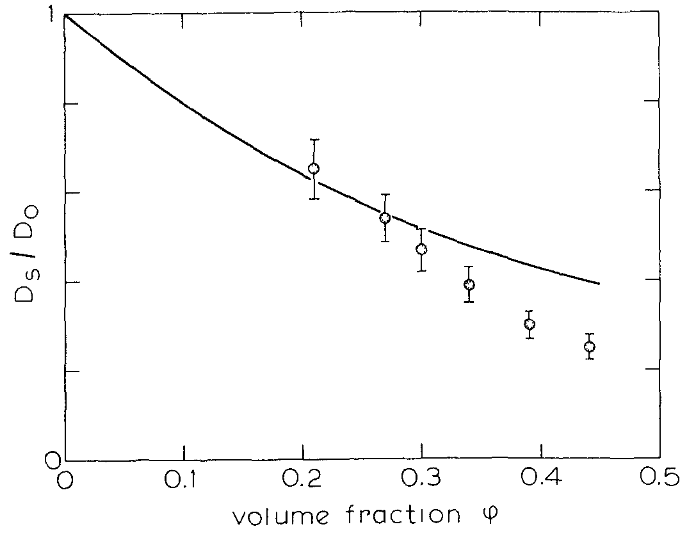

Fig. 1 Volume fraction dependence of D_s/D_o. The theoretical curve is from table 1, the data points are from ref. 13.

results with the virial expansion of D_s (eq. (8.1)). We found from the fluctuation expansion a value of −1.96 for the linear coefficient, in reasonable agreement with the value of −1.73 given in eq. (8.1), or with the *exact* value of −1.83, calculated by Batchelor[3]. In order to obtain also an estimate for the accuracy of the fluctuation expansion at higher densities, we examine the relative magnitude of its first two terms: one sees from table 1 that up to volume fractions of 0.3 the lowest order correction $D_s^{(2)}$ is of the order of 10% (or less) of the zeroth order result $D_s^{(0)}$. One might expect, therefore, that in this regime the concentration dependence of D_s is described reasonably well by our results from the fluctuation expansion. At higher volume fractions, however, the correction $D_s^{(2)}$ becomes more and more important and, consequently, one should expect our results to be increasingly less reliable.

Pusey and van Megen[13] have measured D_s for a concentrated suspension of colloidal latex particles, using dynamic light-scattering techniques. Their data points are also plotted in fig. 1. Unfortunately, a comparison with the virial expansion (8.1) is not possible, since no measurements could be performed at sufficiently low concentrations. As we can see, the fluctuation expansion is in agreement with the experimental data in the regime $\phi \lesssim 0.30$, where we expect our results to be reasonably accurate. However, for $\phi \gtrsim 0.35$ the calculated values for D_s are considerably larger than the measured ones, indicating the importance of higher order terms in the fluctuation expansion. We shall deal with an important class of these terms in the next chapter.

Appendix A. Formulae for irreducible tensors

We shall use the following formulae (cf. ref. 14)

$$\overline{\hat{r}^{n-1}}\,\hat{r} = \overline{\hat{r}^{n}} + \frac{n-1}{2n-1}\,\underline{\Delta}^{(n-1,n-1)} \odot^{n-2} \overline{\hat{r}^{n-2}} \quad , \qquad (A.1)$$

$$\overline{\hat{r}^{n}} \odot^{n} \overline{\hat{r}^{n}} = n!/(2n-1)!! \quad , \qquad (A.2)$$

$$\underline{\Delta}^{(n,n)} \odot^{m} \underline{\Delta}^{(m,m)} = \underline{\Delta}^{(n,n)} \qquad \text{if } m \leq n \quad , \qquad (A.3)$$

$$\underline{\Delta}^{(n,n)} \odot^{m} \underline{\Delta}^{(m,m)} = 0 \qquad \text{if } m > n \quad , \qquad (A.4)$$

$$\underline{\Delta}^{(n,n)} \odot^{n+1} \underline{\Delta}^{(n,n)} = \frac{2n+1}{2n-1}\,\underline{\Delta}^{(n-1,n-1)} \quad , \qquad (A.5)$$

$$\frac{1}{4\pi}\int d\hat{r}\;\overline{\hat{r}^{n}}\;\overline{\hat{r}^{m}} = \delta_{nm}\, n!\,[(2n+1)!!]^{-1}\,\underline{\Delta}^{(n,n)} \quad . \qquad (A.6)$$

Integrals of the form

$$\underline{J}^{(n,m)} \equiv \frac{1}{4\pi}\int d\hat{r}\;\overline{\hat{r}^{n-1}}\,(\underline{1} - \hat{r}\hat{r})\,\overline{\hat{r}^{m-1}} \quad , \quad n,m \geq 2 \quad , \qquad (A.7)$$

can now be evaluated using first eq. (A.1), and then eq. (A.6) and its corollary (cf. definition (2.19))

$$\frac{1}{4\pi}\int d\hat{r}\; \overline{\hat{r}^{n-1}}\;\underline{1}\;\overline{\hat{r}^{m-1}} = \delta_{nm}(n-1)!\,[(2n-1)!!]^{-1}\,\underline{\Delta}^{(n-1,id,n-1)} \quad . \tag{A.8}$$

The result is

$$\underline{J}^{(n,n)} = (n-1)!\,[(2n-1)!!]^{-1}\Big(\underline{\Delta}^{(n-1,id,n-1)} - \frac{n}{2n+1}\,\underline{\Delta}^{(n,n)} - \frac{n-1}{2n-1}\,\underline{\Delta}^{(n-1,n-1)} \odot^{n-2} \underline{\Delta}^{(n-1,n-1)}\Big) \;, \tag{A.9}$$

$$\underline{J}^{(n,n+2)} = \underline{J}^{(n+2,n)} = -\,(n+1)!\,[(2n+3)!!]^{-1}\,\underline{\Delta}^{(n+1,n+1)} \;, \tag{A.10}$$

$$\underline{J}^{(n,m)} = 0 \quad \text{if} \quad n \neq m \quad \text{and} \quad n \neq m \pm 2, \tag{A.11}$$

where we have made use of eq. (A.3) to simplify the expressions.

Appendix B. Proof of equation (6.3)

Every tensor of rank 2, constructed from the tensor $\underline{1}$ and the vector $\hat{r}$, is necessarily of the form $\alpha\,\underline{1} + \beta\,\hat{r}\hat{r}$, with scalars α and β. Hence we can write

$$(\underline{1} - \hat{r}\hat{r})\,\overline{\hat{r}^{n-1}} \odot^{n} \underline{B}^{(n,n)^{-1}} \odot^{n} \overline{\hat{r}^{n-1}}\,(\underline{1} - \hat{r}\hat{r}) = \alpha\,\underline{1} + \beta\,\hat{r}\hat{r}, \quad n \geqslant 3, \tag{B.1}$$

with $\underline{B}^{(n,n)^{-1}}$ $(n \geqslant 3)$ given by eq. (2.22).

If we contract both sides of eq. (B.1) with $\hat{r}$, we find

$$0 = (\alpha + \beta)\,\hat{r} \;, \tag{B.2}$$

hence $\beta = -\alpha$. To determine α we take the trace of eq. (B.1)

$$\sum_{\mu_1\cdots\mu_n}\;\sum_{\nu_1\cdots\nu_n} \delta_{\mu_1\nu_1}\,\overline{\hat{r}_{\mu_2}\cdots\hat{r}_{\mu_n}}\; B^{(n,n)^{-1}}_{\mu_n\cdots\mu_1,\nu_1\cdots\nu_n}\;\overline{\hat{r}_{\nu_n}\cdots\hat{r}_{\nu_2}}$$

$$-\,\hat{r}\,\overline{\hat{r}^{n-1}} \odot^{n} \underline{B}^{(n,n)^{-1}} \odot^{n} \overline{\hat{r}^{n-1}}\,\hat{r} = 2\alpha. \tag{B.3}$$

The l.h.s. of eq. (B.3) can be evaluated with help of the formulae

$$\sum_{\mu_1\cdots\mu_n}\ \sum_{\nu_1\cdots\nu_n}\delta_{\mu_1\nu_1}\overline{\hat{r}_{\mu_2}\cdots\hat{r}_{\mu_n}}\,\Delta^{(n-1,id,n-1)}_{\mu_n\cdots\mu_1,\nu_1\cdots\nu_n}\overline{\hat{r}_{\nu_n}\cdots\hat{r}_{\nu_2}} = 3\,\frac{(n-1)!}{(2n-3)!!}\,, \tag{B.4}$$

$$\sum_{\mu_1\cdots\mu_n}\ \sum_{\nu_1\cdots\nu_n}\delta_{\mu_1\nu_1}\overline{\hat{r}_{\mu_2}\cdots\hat{r}_{\mu_n}}\,\Delta^{(n,n)}_{\mu_n\cdots\mu_1,\nu_1\cdots\nu_n}\overline{\hat{r}_{\nu_n}\cdots\hat{r}_{\nu_2}} = (2n+1)\,\frac{(n-1)!}{(2n-1)!!}\,, \tag{B.5}$$

$$\sum_{\mu_1\cdots\mu_n}\ \sum_{\nu_1\cdots\nu_n}\delta_{\mu_1\nu_1}\overline{\hat{r}_{\mu_2}\cdots\hat{r}_{\mu_n}}\,T^{(n,n)}_{\mu_n\cdots\mu_1,\nu_1\cdots\nu_n}\overline{\hat{r}_{\nu_n}\cdots\hat{r}_{\nu_2}} =$$

$$= \overline{\hat{r}^{n-1}}\odot^{n-1}\overline{\hat{r}^{n-1}} = (n-1)!\,[(2n-3)!!]^{-1}\,, \tag{B.6}$$

$$\hat{r}\,\overline{\hat{r}^{n-1}}\odot^{n}\underline{\Delta}^{(n-1,id,n-1)}\odot^{n}\overline{\hat{r}^{n-1}}\,\hat{r} = \overline{\hat{r}^{n-1}}\odot^{n-1}\overline{\hat{r}^{n-1}} = \frac{(n-1)!}{(2n-3)!!}\,, \tag{B.7}$$

$$\hat{r}\,\overline{\hat{r}^{n-1}}\odot^{n}\underline{\Delta}^{(n,n)}\odot^{n}\overline{\hat{r}^{n-1}}\,\hat{r} = \overline{\hat{r}^{n}}\odot^{n}\overline{\hat{r}^{n}} = \frac{n!}{(2n-1)!!}\,, \tag{B.8}$$

$$\hat{r}\,\overline{\hat{r}^{n-1}}\odot^{n}\underline{T}^{(n,n)}\odot^{n}\overline{\hat{r}^{n-1}}\,\hat{r} = \hat{r}\cdot\overline{\hat{r}^{n-1}}\odot^{n-2}\overline{\hat{r}^{n-1}}\cdot\hat{r} =$$

$$= \left(\frac{n-1}{2n-3}\right)^{2}\overline{\hat{r}^{n-2}}\odot^{n-2}\overline{\hat{r}^{n-2}} = \frac{n-1}{2n-3}\,\frac{(n-1)!}{(2n-3)!!}\,, \tag{B.9}$$

cf. eqs. (A.1)-(A.5)). We have used the abbreviation

$$\underline{T}^{(n,n)} \equiv \underline{\Delta}^{(n-1,n-1)}\odot^{n-2}\underline{\Delta}^{(n-1,n-1)}\ . \tag{B.10}$$

Substitution in eq. (B.1) of the values for α and β which follow from eqs. (B.2)-(B.10) yields

$$(\underline{1}-\hat{r}\hat{r})\hat{r}\,\overline{\hat{r}^{n-1}}\odot^{n}\underline{B}^{(n,n)^{-1}}\odot^{n}\overline{\hat{r}^{n-1}}\,(\underline{1}-\hat{r}\hat{r}) = -[(2n-3)!!]^{-2}(\underline{1}-\hat{r}\hat{r}),\ n\geq 3. \tag{B.11}$$

Since $\underline{B}^{(2,2)^{-1}}$ equals $-\frac{10}{9}\,\underline{\Delta}^{(2,2)}$ (definition (2.6)), a simple calculation gives

$$(\underline{1} - \hat{r}\hat{r})\hat{r} : \underline{B}^{(2,2)^{-1}} : \hat{r}(\underline{1} - \hat{r}\hat{r}) = -\frac{5}{9}(\underline{1} - \hat{r}\hat{r}). \tag{B.12}$$

Eqs. (B.11) and (B.12) give, together with eq. (2.15) the required formula (6.3).

Appendix C. Derivation of equation (6.5)

We wish to calculate the sum

$$\sum_{n=1}^{\infty} (2n+1)^2 J^2_{n+\frac{1}{2}}(x) = 2x^2 \sum_{n=0}^{\infty} [J^2_{n+\frac{1}{2}}(x) + J_{n-\frac{1}{2}}(x)J_{n+3/2}(x)]$$

$$- x^2[J^2_{\frac{1}{2}}(x) + J^2_{3/2}(x) + 2J_{-\frac{1}{2}}(x)J_{3/2}(x)], \tag{C.1}$$

where we have used the recursion relation[15]

$$(2n+1)J_{n+\frac{1}{2}}(x) = xJ_{n-\frac{1}{2}}(x) + xJ_{n+3/2}(x). \tag{C.2}$$

In ref. 24 (§ 116) we find the useful formula

$$\sum_{n=0}^{\infty} J_{n+\nu}(x)J_{n+\rho}(x) = x^{\rho-\nu} \int_0^x t^{\nu-\rho} J_{\nu-1}(t)J_{\rho}(t)\, dt, \tag{C.3}$$

for ν and ρ real numbers. If we take $\nu = \rho = \frac{1}{2}$ we find

$$\sum_{n=0}^{\infty} J^2_{n+\frac{1}{2}}(x) = \pi^{-1} \int_0^{2x} t^{-1}\sin t\, dt \equiv \pi^{-1}\, \mathrm{Si}(2x), \tag{C.4}$$

while the choice $\nu = 3/2$, $\rho = -\frac{1}{2}$ gives

$$\sum_{n=0}^{\infty} J_{n+3/2}(x)J_{n-\frac{1}{2}}(x) = x^{-2}\pi^{-1}\int_0^x t\sin 2t\, dt = x^{-2}\pi^{-1}(\tfrac{1}{4}\sin 2x - \tfrac{1}{2}x\cos 2x). \tag{C.5}$$

Substitution of eqs. (C.4) and (C.5) into (C.1) yields the result

$$\sum_{n=1}^{\infty} (2n+1)^2 J^2_{n+\frac{1}{2}}(x) = \frac{2}{\pi}[x^2\mathrm{Si}(2x) + \tfrac{1}{4}\sin 2x + \tfrac{1}{2}x\cos 2x - x^{-1}\sin^2 x]. \tag{C.6}$$

This is the formula we need in deriving eq. (6.5).

Appendix D. Calculation of $D_s^{(2)}$

We can write the integrals in eq. (7.3) in terms of Fourier transformed renormalized connector fields $\underline{A}_{n_0}^{(n,m)}(\vec{k})$, which, according to eqs. (2.14) and (6.9), are given by

$$\underline{A}_{n_0}^{(n,m)}(\vec{k}) = \underline{A}^{(n,m)}(\vec{k})\ [1 + \phi S(ak)]^{-1}. \tag{D.1}$$

Restricting ourselves to terms in eq. (7.3) containing only connectors with upper indices n,m $\leqslant$ 2, the expression for $\underline{D}_s^{(2)}$ takes the form

$$\begin{aligned}\underline{D}_s^{(2)}/D_0 = {} & n_0(2\pi)^{-3}\int d\vec{k}\ \underline{A}_{n_0}^{(1,2)}(\vec{k}):\underline{B}^{(2,2)^{-1}}:\underline{A}_{n_0}^{(2,2)}(\vec{r}=0):\underline{B}^{(2,2)^{-1}}:\underline{A}_{n_0}^{(2,1)}(\vec{k}) \\ & + n_0(2\pi)^{-6}\int d\vec{k}\int d\vec{k}'\ \underline{A}_{n_0}^{(1,2)}(\vec{k}) : \underline{B}^{(2,2)^{-1}} : \underline{A}_{n_0}^{(2,1)}(\vec{k}')\ \nu(|\vec{k}-\vec{k}'|) \\ & + n_0^2\ (2\pi)^{-6}\int d\vec{k}\int d\vec{k}'\ \underline{A}_{n_0}^{(1,2)}(\vec{k}):\underline{B}^{(2,2)^{-1}}:\underline{A}_{n_0}^{(2,2)}(\vec{k}'):\underline{B}^{(2,2)^{-1}}:\underline{A}_{n_0}^{(2,1)}(\vec{k}) \\ & \times \nu(|\vec{k}-\vec{k}'|),\end{aligned} \tag{D.2}$$

where $\nu(k)$ is the pair correlation function in wave vector representation

$$\nu(k) = \int d\vec{r}\ e^{i\vec{k}\cdot\vec{r}}\ [g(r) - 1]. \tag{D.3}$$

The first integral in eq. (D.2) (due to self-correlations, cf. section 5) can be evaluated with the aid of eqs. (2.6), (2.15) and (6.12)

$$\begin{aligned}\underline{D}_s^{(2)}\ (\textit{self-correlation}) = {} & -\frac{135}{4}\pi\phi^2\underline{1}D_0\int_0^\infty dx\ x^{-4}J_{\frac{1}{2}}^2(x)J_{3/2}^2(x)[1+\phi S(x)]^{-2} \\ & \times\int_0^\infty dy\ y^{-1}J_{3/2}^2(y)\ S(y)[1+\phi S(y)]^{-1}.\end{aligned} \tag{D.4}$$

A numerical integration[21] of these one-dimensional integrals yields the values listed in table 2, column I. The two remaining integrals in eq. (D.2) contain the pair correlation function $\nu(k)$. We have approximated $\nu(k)$ by the solution of the Percus-Yevick equation for hard spheres[22]. (An explicit analytic expression for $\nu(k)$ can be found in ref. 25.) Using eqs. (2.6) and (2.15) we can write the two terms in eq. (D.2) containing pair-correlations as two three-dimensional integrals. These integrals were evaluated by Monte-Carlo integration[19]. The results can also be found in table 2, columns II and III.

Table 2

Specification of the terms contributing to $D_s^{(2)}/D_o$ = I + II + III. The values under I, II and III correspond to the first, second and third term, respectively, on the r.h.s. of eq. (D.2).

ϕ	I	II	III
0.05	- 0.007	+ 0.014	- 0.003
0.10	- 0.019	+ 0.021	- 0.009
0.15	- 0.033	+ 0.024	- 0.014
0.20	- 0.046	+ 0.024	- 0.019
0.25	- 0.057	+ 0.024	- 0.024
0.30	- 0.066	+ 0.022	- 0.027
0.35	- 0.073	+ 0.020	- 0.030
0.40	- 0.079	+ 0.018	- 0.032
0.45	- 0.084	+ 0.016	- 0.034

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CHAPTER III

DIFFUSION:
PARTIAL RESUMMATION OF CORRELATIONS

1. Introduction

In the previous chapter we calculated the concentration dependence of the (short-time) self-diffusion coefficient for spherical particles suspended in a fluid. This quantity, denoted by D_s, is the large-k limit of the wavevector dependent diffusion coefficient D(k), which describes the initial decay of the dynamic structure factor measured by inelastic light- or neutron-scattering[1,2]. In chapter II we resummed the contributions due to hydrodynamic interactions between an arbitrary number of spheres. By including at most two-point correlations between the spheres, we obtained in that chapter a reasonable agreement with experimental results[3] for D_s for volume fractions $\phi \lesssim 0.3$. At higher concentrations the calculated values were too large, indicating the importance of higher order correlations.

The purpose of this chapter is twofold: i) we extend the formalism to diffusion at arbitrary values of the wavevector; ii) we resum to all orders the contributions from a special class of correlations.

The (short-time) wavevector dependent diffusion coefficient D(k) may be expressed in terms of the mobilities of the spheres[1]. To linear order in the density only two-sphere hydrodynamic interactions need to be considered and results for D(k) to this order have been obtained by Russel and Glendinning[4] and by Fijnaut[5]. In a suspension which is not dilute, however, it is essential to fully take into account the many-body hydrodynamic interactions between an arbitrary number of spheres, as we have seen in the previous chapter. Using general expressions for many-sphere mobilities obtained by Mazur and van Saarloos[6], we shall give in section 2 a formula for the diffusion coefficient which is a convenient starting point for the calculation of D(k) in a concentrated suspension, through an expansion in density-fluctuation correlation functions of increasing order. Such a "fluctuation expansion", in which the many-sphere hydrodynamic interactions are resummed algebraically, was employed in ch. II also (for the case of self-diffusion). In this chapter we shall - in addition - resum to all orders the contributions from a class of self-correlations, cf. sections 3, 4 and 5. Results for the concentration and wavevector dependence of D(k) are given in section 6, and are compared with experimental data[3,7,8]. We conclude this chapter in section 7 with an interpretation of our results in terms of an *effective* pair-mobility.

2. An operator expression for D(k)

As in ch. II we study a system of N spherical particles with radius a and position vectors $\vec{R}_i$ $(i = 1,2,\ldots N)$, suspended in a liquid with viscosity η. *While in our previous analysis we restricted ourselves* to the self-diffusion coefficient D_s of the suspended particles, we shall consider here the wavevector dependent diffusion coefficient D(k), given by (see e.g. ref. 1 and ch. I)

$$D(k) = k_B T[NG(k)]^{-1} \sum_{i,j=1}^{N} \langle \hat{k}\cdot\underline{\mu}_{ij}\cdot\hat{k}\; e^{i\vec{k}\cdot\vec{R}_{ij}}\rangle. \tag{2.1}$$

Here $\vec{k}$ is the wavevector with magnitude k and direction $\hat{k} \equiv \vec{k}/k$, G(k) is the static structurefactor, $\underline{\mu}_{ij}$ is a mobility tensor, $\vec{R}_{ij} \equiv \vec{R}_j - \vec{R}_i$, and k_B and T denote Boltzmann's constant and the temperature respectively. The angular brackets denote an average over the configurations of the spheres in a volume V.

The quantity defined in eq. (2.1) describes diffusion of the spheres on a time scale over which their positions are essentially constant[1]. It can be measured by light-scattering, and is called in this context the "effective" diffusion coefficient[2]. The (short-time) self-diffusion coefficient D_s, studied in ch. II, is given by

$$D_s \underline{1} = k_B T N^{-1} \sum_{i=1}^{N} \langle \underline{\mu}_{ii} \rangle . \qquad (2.2)$$

It is the large wavevector limit of D(k)

$$D_s = \lim_{k \to \infty} D(k), \qquad (2.3)$$

as can be understood by noting that

$$\lim_{k \to \infty} G(k) = 1 \qquad (2.4)$$

and that in the limit $k \to \infty$ only the terms with $i=j$ contribute to the average in equation (2.1). Note furthermore that, in an isotropic suspension, the average in eq. (2.2) is proportional to the unit tensor $\underline{1}$.

General expressions for the many-sphere mobility tensors $\underline{\mu}_{ij}$ were derived by Mazur and van Saarloos[6]. It is convenient to write these results in the compact operator notation used in ch. II. To this end we express the mobilities in terms of an operator kernel $\underline{\mu}(\vec{r}\,|\vec{r}\,')$, by

$$6\pi\eta a \underline{\mu}_{ij} = \underline{1}\delta_{ij} + \int d\vec{r} \int d\vec{r}\,' \; \delta(\vec{r} - \vec{R}_i)\delta(\vec{r}\,' - \vec{R}_j)\underline{\mu}(\vec{r}\,|\vec{r}\,'). \qquad (2.5)$$

We further define the microscopic number density $n(\vec{r})$ of the spheres

$$n(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{R}_i). \qquad (2.6)$$

Eq. (2.1) then takes the form

$$G(k)D(k)/D_o = 1 + N^{-1}\int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}} \int d\vec{r}\,' e^{i\vec{k}\cdot\vec{r}\,'} \langle \hat{k}\cdot n(\vec{r})\underline{\mu}(\vec{r}\,|\vec{r}\,')n(\vec{r}\,')\cdot\hat{k} \rangle, \qquad (2.7)$$

or, defining the operators $\underline{\mu}$ with kernel $\underline{\mu}(\vec{r}\,|\vec{r}\,')$ and n with kernel $n(\vec{r})\delta(\vec{r}\,' - \vec{r})$,

$$G(k)D(k)/D_o = 1 + N^{-1}\langle\hat{k}\cdot\{n\underline{\mu}n\}(\vec{k}\,|\vec{k})\cdot\hat{k}\rangle. \qquad (2.8)$$

In this last equation we have defined the Fourier transform of an operator kernel $C(\vec{r}\,|\vec{r}\,') \equiv \{n\underline{\mu}n\}(\vec{r}\,|\vec{r}\,')$ as

$$C(\vec{k}\,|\vec{k}\,') \equiv \int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}} \int d\vec{r}\,'\; e^{i\vec{k}\,'\cdot\vec{r}\,'}\, C(\vec{r}\,|\vec{r}\,'). \qquad (2.9)$$

The Stokes-Einstein diffusion coefficient is denoted by

$$D_o = k_B T(6\pi\eta a)^{-1}. \qquad (2.10)$$

Adopting the notation of ch. II (cf. eqs. (II-3.4), (II-3.10)-(II-3.13)), expression (II-2.2) for the mobility tensors takes for the operator $\underline{\mu}$ the compact form

$$\underline{\mu} = \mathit{PA}\,(\mathit{1} - n\,\mathit{QB}^{-1}\mathrm{A}\,)^{-1}\mathrm{P}\,, \qquad (2.11)$$

and we thus finally obtain for the diffusion coefficient the expression

$$G(k)D(k)/D_o = 1 + N^{-1}\langle\hat{k}\cdot\{\mathit{P}\,n\mathit{A}\,(\mathit{1} - n\,\mathit{QB}^{-1}\mathrm{A}\,)^{-1}n\mathit{P}\,\}(\vec{k}\,|\vec{k})\cdot\hat{k}\rangle. \qquad (2.12)$$

Expression (2.12) for the diffusion coefficient D(k) is exact and fully contains the many-body hydrodynamic interactions between the N spheres. It is the required extension of the formula for the self-diffusion coefficient D_s given in ch. II, eq. (II-3.16). As we have shown there - and will see again in the next section - such formal operator expressions are very useful in a study of concentrated suspensions.

3. Renormalization of the connectors

Let $\underline{\gamma}_o^{(m,m)}$ (m = 1,2,3,...) be an arbitrary constant tensor of rank 2m. We denote by γ_o the diagonal matrix with elements

$$\{\gamma_o\}_{n,m} = \delta_{nm}\, \underline{\gamma}_o^{(m,m)}. \qquad (3.1)$$

A matrix of *renormalized connectors* $\mathcal{A}_{\gamma_o}$ is defined – for each γ_o – as

$$\mathcal{A}_{\gamma_o} \equiv \mathcal{A}\,(\mathcal{1} - \gamma_o\, \mathcal{QB}^{-1}\, \mathcal{A})^{-1}. \qquad (3.2)$$

The n,m element of the matrix $\mathcal{A}_{\gamma_o}$ is a renormalized connector $\underline{A}_{\gamma_o}^{(n,m)}$, which in turn is a convolution operator with kernel $\underline{A}_{\gamma_o}^{(n,m)}(\vec{r})$.

We now choose $\underline{\gamma}_o^{(m,m)}$ to be a function of the average number density of the spheres $n_o = N/V$,

$$\underline{\gamma}_o^{(1,1)} = n_o\, \underline{1},$$

$$\underline{\gamma}_o^{(m,m)} - \underline{\gamma}_o^{(m,m)} \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{\gamma_o}^{(m,m)}(\vec{r}=0) = n_o\, \underline{1}^{(m,m)}, \quad m \geqslant 2. \qquad (3.3)$$

The tensor $\underline{1}^{(m,m)}$ used in this equation is a generalized unit tensor of rank 2m,

$$\underline{1}^{(2,2)} = \underline{\Delta}^{(2,2)}, \quad \underline{1}^{(m,m)} = \underline{\Delta}^{(m-1,id,m-1)} \quad (m \geqslant 3), \qquad (3.4)$$

where the $\underline{\Delta}$-tensors are defined in eqs. (II-2.9) and (II-2.19). The *renormalized "density"* $\gamma(\vec{r})$, with average γ_o, is given by

$$\gamma(\vec{r}) \equiv \gamma_o n_o^{-1} n(\vec{r}); \qquad (3.5)$$

the corresponding diagonal operator γ has kernel $\gamma(\vec{r})\delta(\vec{r}\,' - \vec{r})$. The renormalized density and connectors defined above will be explicitly evaluated in section 4.

In ch. II we defined renormalized connectors $\mathcal{A}_{n_o}$ according to eq. (3.2), with γ_o replaced by n_o, and used the identity

$$\mathcal{A}\,(\mathcal{1} - n\, \mathcal{QB}^{-1} \mathcal{A})^{-1} n = \mathcal{A}_{n_o}(\mathcal{1} - \delta n\, \mathcal{QB}^{-1}\, \mathcal{A}_{n_o})^{-1} n, \qquad (3.6)$$

where $\delta n \equiv n - n_o$ denotes the density fluctuations. If one substitutes this identity into eq. (2.12) and expands the operator between braces in this equation in powers of δn, one obtains an expansion for D(k) in correlation functions of density fluctuations of higher and higher order (a socalled fluctuation expansion). For the case of self-diffusion, this expansion was evaluated to second order in ch. II. The renormalized connectors $\mathcal{A}_{n_0}$ account for a full resummation of the many-body hydrodynamic interactions in the absence of correlations, and in this way for the fact that (in some averaged sense) spheres interact hydrodynamically via a suspension with density n_0, rather than through the pure fluid. As we shall shortly see, the renormalization of the density, defined in eq. (3.3), will moreover account for a partial resummation of correlations.

The following identity will prove very useful in our analysis

$$\mathcal{A}\,(\mathit{1} - n\,\mathcal{QB}^{-1}\mathcal{A}\,)^{-1}n = \mathcal{A}_{\gamma_0}(\mathit{1} - \delta\gamma\,\mathcal{QB}^{-1}\,\overset{o}{\mathcal{A}}_{\gamma_0})^{-1}\gamma. \qquad (3.7)$$

This formula differs from the previous one (eq. (3.6)) in that it contains the renormalized density γ, density fluctuations $\delta\gamma \equiv \gamma - \gamma_0$ and cut-out connectors $\overset{o}{\underline{A}}{}^{(n,m)}_{\gamma_0} = \{\,\overset{o}{\mathcal{A}}_{\gamma_0}\}_{n,m}$ with kernels

$$\overset{o}{\underline{A}}{}^{(n,m)}_{\gamma_0}(\vec{r}\,|\vec{r}\,') = \overset{o}{\underline{A}}{}^{(n,m)}_{\gamma_0}(\vec{r}\,'-\vec{r}\,) = \begin{cases} 0 \text{ if } \vec{r} = \vec{r}\,' \text{ and } n = m, \\ \underline{A}^{(n,m)}_{\gamma_0}(\vec{r}\,'-\vec{r}\,) \text{ if } \vec{r} \neq \vec{r}\,' \text{ or } n \neq m. \end{cases} \qquad (3.8)$$

A proof of eq. (3.7) is given in the appendix of this chapter. Substituting this identity into expression (2.12) for D(k) one finds

$$G(k)D(k)/D_0 = 1 + N^{-1}\langle\hat{k}\cdot\{\,\mathcal{P}n\mathcal{A}_{\gamma_0}(\,\mathit{1} - \delta\gamma\,\mathcal{QB}^{-1}\,\overset{o}{\mathcal{A}}_{\gamma_0})^{-1}n\mathcal{P}\,\}(\vec{k}|\vec{k})\cdot\hat{k}\rangle, \quad (3.9)$$

where use has been made of the fact that $\gamma\mathcal{P} = n\mathcal{P}$, in view of definitions (3.3) and (3.5).

If one expands the operator between braces in eq. (3.9) in powers of $\delta\gamma$ one obtains again an expansion for D(k) in density fluctuation correlation functions, since $\delta\gamma = \gamma_0 n_0^{-1}\delta n$ (cf. eq. (3.5)) is linear in the density fluctuations δn. The $\delta\gamma$-expansion differs, however, from the δn-expansion considered in ch. II, in that the contributions from a special class of correlations (which we call *ring self-correlations*) are in the former expansion included in the lowest order term. Indeed each term in the δγ-expansion may be obtained by partial resummation of the δn-expansion.

The difference between these two expansions of the diffusion coefficient may be understood as follows. An s-point correlation $\langle\delta n(\vec{r}_1)\delta n(\vec{r}_2)\ldots\delta n(\vec{r}_s)\rangle$ contains many terms which are proportional to delta functions $\delta(\vec{r}_k - \vec{r}_\ell)$ $(k,\ell = 1,2,\ldots,s;\ k \neq \ell)$. For $s = 2$ one has e.g.

$$\langle\delta n(\vec{r}_1)\delta n(\vec{r}_2)\rangle = n_o\delta(\vec{r}_2 - \vec{r}_1) + n_o^2\,[g(|\vec{r}_2 - \vec{r}_1|)-1], \qquad (3.10)$$

where the delta function term represents the self-correlation and g(r) is the pair distribution function. As a consequence of self-correlations, an expression of the form $\langle(\delta n_{n_o})^s\rangle$ contains a class of contributions with factors $\underline{A}_{n_o}^{(m,k)}(\vec{r}=0)$ $(m,k = 1,2,3,\ldots)$. Referring to a diagrammatic representation, this factor is called a ring self-correlation. We remark that a contribution from these ring self-correlations is most important when the upper indices m and k of the factor $\underline{A}_{n_o}^{(m,k)}(\vec{r}=0)$ are equal*. In this case we speak of *diagonal* ring self-correlations.

Similarly, an s-th order correlation between *renormalized* density fluctuations $\langle(\delta\overset{o}{\gamma}_{\gamma_o})^s\rangle$ would contain terms with factors $\underline{A}_{\gamma_o}^{o(m,k)}(\vec{r}=0)$. However, in view of definition (3.8) of the cut-out connector field, these terms are zero, unless $m \neq k$. For this reason the various terms in the δγ-expansion do not contain diagonal ring self-correlations. The contributions of these have been resummed algebraically by the renormalization of the density through eq. (3.3).

To conclude this section we give the expression for the self-diffusion coefficient D_s, which follows from eq. (II-3.16) with the

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*For example, the contribution (of second order in δn) to the self-diffusion coefficient from the term with the factor $\underline{A}_{n_o}^{(2,2)}(\vec{r}=0)$ is $-0.084D_o$, at the highest density considered in ch.II (cf. table 2). At the same density, the term with the factor $\underline{A}_{n_o}^{(1,3)}(\vec{r}=0)$ contributes only $-0.002D_o$.

use of identity (3.7),

$$\underline{1}D_s/D_o = \underline{1} + n_o^{-1}\langle\{ \quad {}_{\gamma_o}(\quad - \delta\gamma \quad {}^{-1} \, {}^{o} \, {}_{\gamma_o})^{-1} n \quad \}(\vec{r}|\vec{r})\rangle . \tag{3.11}$$

Note that, due to translational invariance, the r.h.s. of this equation is independent of $\vec{r}$. We recall that, as indicated in section 2, D_s is also the large wavevector limit of $D(k)$, given by eq. (3.9). One must realize, however, that if one first expands the r.h.s. of eq. (3.9) in correlation functions of δn of higher and higher order, this series expansion is not equal term by term, in the limit $k \to \infty$, to the corresponding series expansion of eq. (3.11). We shall return to this point in section 5.

4. Evaluation of the renormalized connectors

In order to solve eq. (3.3) for γ_o we make the following "Ansatz"

$$\underline{\gamma}_o^{(m,m)} = \gamma_o^{(m)} \, \underline{1}^{(m,m)}, \quad m \geq 2, \tag{4.1}$$

where $\gamma_o^{(m)}$ is a scalar function of the density n_o. As we shall see, this is indeed the form of the solution. The generalized unit tensor $\underline{1}^{(m,m)}$ was defined in eq. (3.4) and has the property that

$$\underline{1}^{(m,m)} \odot \underline{B}^{(m,m)^{-1}} = \underline{B}^{(m,m)^{-1}} . \tag{4.2}$$

The evaluation of the renormalized connector field $\underline{A}_{\gamma_o}^{(n,m)}(\vec{r})$, defined in section 3, then proceeds entirely as the evaluation of $\underline{A}_{n_o}^{(n,m)}(\vec{r})$ in ch. II, section 6, and gives

$$\underline{A}_{\gamma_o}^{(n,m)}(\vec{r}) = \underline{\tilde{A}}^{(n,m)}(\vec{r}) - (2\pi)^{-3}\int d\vec{k}\, e^{-i\vec{k}\cdot\vec{r}}\, \underline{A}^{(n,m)}(\vec{k})$$

$$\times\, \phi S_{\gamma_o}(ak)[1 + \phi S_{\gamma_o}(ak)]^{-1} . \tag{4.3}$$

Here $\phi = \frac{4}{3}\pi a^3 n_o$ is the volume fraction of the spheres and the function $S_{\gamma_o}(ak)$ is given as an infinite sum of Bessel functions

$$S_{\gamma_o}(ak) = \sum_{p=2}^{\infty} \frac{9}{4}\pi\varepsilon_p\gamma_o^{(p)} n_o^{-1} (2p-1)^2 (ak)^{-3} J^2_{p-\frac{1}{2}}(ak). \qquad (4.4)$$

We have defined $\varepsilon_2 = 5/9$, $\varepsilon_p = 1$ $(p \geqslant 3)$. The case considered in ch. II corresponds to $\gamma_o^{(p)} \equiv n_o$ for all p. The series in eq. (4.4) can then be summed analytically and gives the function S(ak) defined in eq. (II-6.6).

To calculate the density dependence of γ_o, given by eq. (3.3), we need the result

$$\underline{B}^{(m,m)^{-1}} \odot \underline{A}_{\gamma_o}^{(m,m)}(\vec{r}=0) = \underline{1}^{(m,m)}(2m-1)\int_0^\infty dk\, k^{-1} J^2_{m-\frac{1}{2}}(k)\phi S_{\gamma_o}(k) \times [1+\phi S_{\gamma_o}(k)]^{-1}, \quad m \geqslant 2, \qquad (4.5)$$

and for later use also

$$\underline{A}_{\gamma_o}^{(1,1)}(\vec{r}=0) = -\underline{1}\int_0^\infty dk\, k^{-1} J^2_{\frac{1}{2}}(k)\phi S_{\gamma_o}(k)[1+\phi S_{\gamma_o}(k)]^{-1}, \qquad (4.6)$$

$$\underline{A}_{\gamma_o}^{(m,m+2)}(\vec{r}=0) = \underline{A}_{\gamma_o}^{(m+2,m)}(\vec{r}=0) = -\frac{3}{2}(m+1)!(2m-1)!!\,\underline{\Delta}^{(m+1,m+1)} \times \int_0^\infty dk\, k^{-1} J_{m-\frac{1}{2}}(k) J_{m+3/2}(k)\phi S_{\gamma_o}(k)[1+\phi S_{\gamma_o}(k)]^{-1}, \qquad (4.7)$$

$$\underline{A}_{\gamma_o}^{(n,m)}(\vec{r}=0) = 0, \text{ if } n \neq m \text{ and } n \neq m \pm 2. \qquad (4.8)$$

Here $(2m-1)!! = 1\cdot3\cdot5\cdot\ldots\cdot(2m-3)\cdot(2m-1)$; the $\underline{\Delta}$-tensors are defined in eq. (II-2.9). Eqs. (4.5)-(4.8) are the analoga of eqs. (II-6.11)-(II-6.14) for $\underline{A}_{n_o}^{(n,m)}(\vec{r}=0)$, and are obtained by performing the angular integration in eq. (4.3), using the explicit expressions for $\underline{A}^{(n,m)}(\vec{k})$.

Substitution of formula (4.5) into eq. (3.3) shows that γ_o is indeed of the form (4.1) and gives for the scalar functions $\gamma_o^{(m)}$ the equations

$$\gamma_0^{(m)} - \gamma_0^{(m)} \phi(2m-1)\int_0^\infty dk\; k^{-1} J^2_{m-\frac{1}{2}}(k) S_{\gamma_0}(k)[1+\phi S_{\gamma_0}(k)]^{-1} = n_0, \quad m=2,3,\ldots \qquad (4.9)$$

One sees that $\gamma_0^{(m)}$ differs from n_0 by terms of order ϕ^2.

In order to solve the infinite set of coupled equations (4.9) to a sufficient accuracy we approximate the function $S_{\gamma_0}(k)$ by

$$S^{(L)}_{\gamma_0}(k) \equiv S(k) + \sum_{p=2}^{L} \frac{9}{4}\pi\varepsilon_p\left(\gamma_0^{(p)} - n_0\right)n_0^{-1}\,(2p-1)^2\,k^{-3} J^2_{p-\frac{1}{2}}(k), \qquad (4.10)$$

for a given number L = 2,3,... . From the definition of S(k) (eq. (II-6.6)) and $S_{\gamma_0}(k)$ (eq. (4.4)) it follows that

$$\lim_{L\to\infty} S^{(L)}_{\gamma_0}(k) = S_{\gamma_0}(k). \qquad (4.11)$$

With the above approximation the L-1 equations for $\gamma_0^{(m)}$ ($m = 2,3,..,L$) in (4.9) decouple and may be solved numerically*. We give in table 1, for volume fractions ϕ up to 0.45, the values of $\phi\gamma_0^{(m)}/n_0$ ($m = 2,3,4,5$) obtained by this procedure with L = 5.

To calculate the diffusion coefficient D(k) we shall in the next section use these values for $\gamma_0^{(m)}$; also, in expression (4.3) for $\underline{A}^{(n,m)}_{\gamma_0}(\vec{r})$, we shall approximate $S_{\gamma_0}(ak)$ by $S^{(5)}_{\gamma_0}(ak)$, as defined in eq. (4.10). An estimate of the error resulting from this approximation can be obtained by repeating the calculation of γ_0 described above to a lower order. In table 2 we give for $\phi = 0.40$ the values of $\phi\gamma_0^{(m)}/n_0$ ($2<m<L$) and $\underline{1} + \underline{A}^{(1,1)}_{\gamma_0}(\vec{r}$=0), obtained from this calculation with L ranging from 2 to 5. One finds, in particular, that by increasing the order L from 4 to 5, the change in $\gamma_0^{(m)}$ ($m = 2,3,4$) is smaller than 3%, while the value of $\underline{1} + \underline{A}^{(1,1)}_{\gamma_0}(\vec{r}$=0) changes by even less. This last quantity is equal to the large wavevector limit of D(k), to lowest order in the expansion in correlation functions, cf. section 5. Moreover, it has been checked that also for smaller wavevectors use of $S^{(4)}_{\gamma_0}$ instead of $S^{(5)}_{\gamma_0}$ would change the (lowest order) results for D(k) by not more than 2%.

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*Use was made of numerical algorithms from the NAG library (Oxford).

Table 1

Values of the scalar functions $\phi\gamma_o^{(m)}/n_o$ (m = 2,3,4 and 5) for nine different volumefractions ϕ.

	$\phi\gamma_o^{(m)}/n_o$			
ϕ	m=2	m=3	m=4	m=5
0.05	0.0553	0.0542	0.0533	0.0525
0.10	0.1228	0.1177	0.1135	0.1104
0.15	0.2048	0.1918	0.1813	0.1738
0.20	0.3038	0.2777	0.2574	0.2432
0.25	0.4224	0.3766	0.3423	0.3186
0.30	0.5627	0.4895	0.4364	0.4005
0.35	0.7267	0.6172	0.5402	0.4888
0.40	0.9157	0.7601	0.6538	0.5839
0.45	1.1310	0.9183	0.7776	0.6856

Table 2

Values of $\phi\gamma_o^{(m)}/n_o$ ($2 \leqslant m \leqslant L$) for $\phi = 0.40$, obtained by solving eq. (4.9) with the approximation of S_{γ_o} by $S_{\gamma_o}^{(L)}$ (eq. (4.10)). The order L of this approximation is increased from 2 to 5, the value L = 5 giving the results presented in the previous table for the whole range of volume fractions. Also shown, for $\phi = 0.40$, is the convergence of the quantity $\underline{1} + \underline{A}_{\gamma_o}^{(1,1)}(\vec{r}=0)$, as the order of the approximation increases.

	$\phi\gamma_o^{(m)}/n_o$	($\phi = 0.40$)			
L	m=2	m=3	m=4	m=5	$\underline{1} + \underline{A}_{\gamma_o}^{(1,1)}(\vec{r}=0)$
2	0.783				0.397 $\underline{1}$
3	0.868	0.711			0.363 $\underline{1}$
4	0.901	0.745	0.637		0.353 $\underline{1}$
5	0.916	0.760	0.654	0.584	0.348 $\underline{1}$

We thus conclude that the approximation made by replacing S_{γ_o} by $S^{(5)}_{\gamma_o}$ (defined in eq. (4.10)) is for present purposes sufficiently accurate.

5. Expansion of D(k) in correlation functions of renormalized density fluctuations

We now return to the formal expression (3.9) for the wavevector dependent diffusion coefficient. We first note that we may replace the two density operators n in this expression by their fluctuations $\delta n = n - n_o$. The terms containing the average n_o do not contribute, in view of the fact that

$$\hat{k}\cdot\int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}}\,\underline{A}^{(1,m)}_{\gamma_o}(\vec{r}\,'-\vec{r}) = \int d\vec{r}\; e^{i\vec{k}\cdot\vec{r}}\,\underline{A}^{(1,m)}_{\gamma_o}(\vec{r}-\vec{r}\,')\cdot\hat{k} = 0. \qquad (5.1)$$

Indeed these integrals are proportional to either $\hat{k}\cdot\underline{A}^{(1,m)}(\vec{k})$ or to $\underline{A}^{(m,1)}(\vec{k})\cdot\hat{k}$ (cf. eq. (4.3)*), both of which quantities are zero for all m, as follows from eq. (II-2.15). The resulting *exact* expression for the diffusion coefficient D(k)

$$G(k)D(k)/D_o = 1 + N^{-1}\langle\hat{k}\cdot\{\,\mathcal{P}\,\delta n\,A_{\gamma_o}(\,\mathcal{1}-\delta\gamma\;\mathcal{QB}^{-1}\,\overset{o}{A}_{\gamma_o})^{-1}\delta n\;\mathcal{P}\}(\vec{k}|\,\vec{k})\cdot\hat{k}\rangle, \qquad (5.2)$$

is the starting point for an expansion of this quantity in correlation functions of renormalized density fluctuations $\delta\gamma$ of higher and higher order.

To lowest order in $\delta\gamma$ one has

$$G(k)D(k)/D_o = 1 + N^{-1}\langle\hat{k}\cdot\{\delta n\underline{A}^{(1,1)}_{\gamma_o}\,\delta n\}(\vec{k}|\,\vec{k})\cdot\hat{k}\rangle. \qquad (5.3)$$

In $\vec{r}$-representation the two-point correlation in this equation can be

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*Note that if expression (4.3) for $\underline{A}^{(n,m)}_{\gamma_o}(\vec{r})$ is substituted into eq. (5.1), one may replace the connector field $\underset{\sim}{\tilde{A}}^{(n,m)}(\vec{r})$ in this expression by $\underline{A}^{(n,m)}(\vec{r})$, since these two connector fields differ by a finite amount in a single point only (cf. eq. (II-3.4)).

written as the sum of a self- and a pair-correlation (cf. eq. (3.10))

$$\langle\{\delta n \underline{A}^{(1,1)}_{\gamma_o} \delta n\}(\vec{r}|\vec{r}\,')\rangle = n_o \underline{A}^{(1,1)}_{\gamma_o}(\vec{r}=0)\delta(\vec{r}\,'-\vec{r}) + n_o^2 \underline{A}^{(1,1)}_{\gamma_o}(\vec{r}\,'-\vec{r})$$

$$\times [g(|\vec{r}\,'-\vec{r}|) - 1], \qquad (5.4)$$

where g(r) is the pair distribution function. Transforming to wavevector representation according to eq. (2.9) one therefore finds for D(k) to lowest order

$$G(k)D(k)/D_o = 1 + \hat{k}\cdot\underline{A}^{(1,1)}_{\gamma_o}(\vec{r}=0)\cdot\hat{k}$$
$$+ n_o \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \hat{k}\cdot\underline{A}^{(1,1)}_{\gamma_o}(\vec{r})\cdot\hat{k}\, [g(r)-1]. \qquad (5.5)$$

To evaluate this expression we used (as in ch. II, cf. appendix D) the Percus-Yevick approximation for the Fourier transform of the pair correlation function

$$\nu(k) \equiv \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}[g(r)-1]. \qquad (5.6)$$

The structurefactor G(k), defined as

$$G(k) = 1 + n_o\nu(k), \qquad (5.7)$$

was calculated in the same approximation*.

The first two terms on the r.h.s. of eq. (5.5) are wavevector independent; from eq. (4.6) one finds

$$1 + \hat{k}\cdot\underline{A}^{(1,1)}_{\gamma_o}(\vec{r}=0)\cdot\hat{k} = \frac{2}{\pi}\int_0^\infty dx(\sin x/x)^2[1+\phi S_{\gamma_o}(x)]^{-1}. \qquad (5.8)$$

The function $S_{\gamma_o}(x)$ was discussed in the last section. The third term on the r.h.s. of eq. (5.5) is, according to eq. (4.3) (cf. also the first footnote of this section), given by

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*For the value of G(k) at k = 0, however, we used the slightly more accurate formula of Carnahan and Starling[9].

$$n_0\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \hat{k}\cdot\underline{A}^{(1,1)}_{\gamma_0}(\vec{r})\cdot\hat{k}[g(r)-1] = n_0(2\pi)^{-3}\int d\vec{k}'\hat{k}\cdot\underline{A}^{(1,1)}(\vec{k}')\cdot\hat{k}$$

$$\times\ [1+\phi S_{\gamma_0}(ak')]^{-1}\nu(|\vec{k}-\vec{k}'|), \qquad (5.9)$$

where (cf. eq. (II-2.15))

$$n_0\ \underline{A}^{(1,1)}(\vec{k}) = \frac{9}{2}\ \phi(ak)^{-4}\sin^2(ak)(\underline{1}-\hat{k}\hat{k}). \qquad (5.10)$$

The results from a numerical integration of these equations will be given in the next section. We note that for large wavevectors k the integral (5.9) goes to zero and only the contribution (5.8) to the diffusion coefficient remains, which in this limit represents the self-diffusion coefficient.

From eq. (5.2) one sees that the first correction to the result (5.3) for D(k) is due to three-point correlations between renormalized density fluctuations. In general this correction will therefore contain the three-sphere correlation function and is difficult to evaluate. Nevertheless, an indication of the accuracy of our lowest order result for D(k) can be obtained by calculating the self-diffusion coefficient D_s to higher order. Indeed D_s contributes to D(k) at all wavevectors,

$$G(k)D(k) = D_s + k_BTN^{-1}\sum_{i\neq j}\langle\hat{k}\cdot\underline{\mu}_{ij}\cdot\hat{k}\ e^{i\vec{k}\cdot\vec{R}_{ij}}\rangle, \qquad (5.11)$$

(cf. eqs. (2.1) and (2.2)), and is in fact the largest of the two terms on the r.h.s. of eq. (5.11), over the whole range of wavevectors and densities. For this reason we shall in the remaining part of this section focus our attention on the self-diffusion coefficient, given by eq. (3.11).

Upon expansion of eq. (3.11) for D_s in correlations of renormalized density fluctuations, one finds for the zeroth order term $D_s^{(0)}$

$$\underline{1}\ D_s^{(0)}/D_0 = \underline{1} + \underline{A}^{(1,1)}_{\gamma_0}(\vec{r}=0). \qquad (5.12)$$

The r.h.s. of this equation is identical to eq. (5.8); the lowest order term therefore in the expansion of formula (3.11) for D_s is equal to the limit k → ∞ of the lowest order term in the expansion of eq. (3.9) for D(k). This correspondence, however, does not exist term by term for higher order terms. (See *in this connection the remark* after eq. (3.11).) The values of $D_s^{(0)}$ (resulting from a numerical integration of the integral in eq. (5.8)*) are shown in table 3, for various volume fractions up to $\phi = 0.45$.

The lowest order correction $D_s^{(2)}$ to $D_s^{(0)}$ results from two-point correlations; it is given by (cf. eq. (3.11))

$$\underline{1}D_s^{(2)}/D_o = n_o^{-1}\,\mathcal{P}\langle\{ A_{\gamma_o}\,\delta\gamma\,\mathcal{QB}^{-1}\,\overset{\circ}{A}_{\gamma_o}\,\delta n + A_{\gamma_o}\,\delta\gamma\,\mathcal{QB}^{-1}\,\overset{\circ}{A}_{\gamma_o}\,\delta\gamma\,\mathcal{QB}^{-1}\,\overset{\circ}{A}_{\gamma_o}\,n_o\}(\vec{r}|\,\vec{r})\rangle\mathcal{P} \,, \qquad (5.13)$$

or, written out explicitly (cf. eqs. (3.5), (3.8), (3.10), (4.1) and (4.2))

$$\underline{1}D_s^{(2)}/D_o = \gamma_o^{(3)}\,n_o^{-1}\,\underline{A}_{\gamma_o}^{(1,3)}(\vec{r}=0)\odot\underline{B}^{(3,3)^{-1}}\odot\underline{A}_{\gamma_o}^{(3,1)}(\vec{r}=0) +$$

$$+\,2\sum_{m=2}^{\infty}\gamma_o^{(m)}\,\gamma_o^{(m+2)}\,n_o^{-1}\int d\vec{r}\,\underline{A}_{\gamma_o}^{(1,m)}(\vec{r})\odot\underline{B}^{(m,m)^{-1}}\odot\underline{A}_{\gamma_o}^{(m,m+2)}(\vec{r}=0)\odot$$

$$\odot\,\underline{B}^{(m+2,m+2)^{-1}}\odot\underline{A}_{\gamma_o}^{(m+2,1)}(-\vec{r}) + \sum_{m=2}^{\infty}\gamma_o^{(m)}\int d\vec{r}\,\underline{A}_{\gamma_o}^{(1,m)}(\vec{r})\odot\underline{B}^{(m,m)^{-1}}\odot$$

$$\odot\,\underline{A}_{\gamma_o}^{(m,1)}(-\vec{r})[g(r)-1] + \sum_{m=2}^{\infty}\sum_{k=2}^{\infty}\gamma_o^{(m)}\,\gamma_o^{(k)}\int d\vec{r}\int d\vec{r}\,'\underline{A}_{\gamma_o}^{(1,m)}(\vec{r})\odot\underline{B}^{(m,m)^{-1}}\odot$$

$$\odot\,\underline{A}_{\gamma_o}^{(m,k)}(\vec{r}\,'-\vec{r})\odot\underline{B}^{(k,k)^{-1}}\odot\underline{A}_{\gamma_o}^{(k,1)}(-\vec{r}\,')[g(|\vec{r}\,'-\vec{r}|)-1]. \qquad (5.14)$$

To simplify this expression we have also used eqs. (4.7) and (4.8). The above eqs. (5.12)-(5.14) are the analoga of eqs. (II-5.7),(II-5.9)

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*With the approximation of S_{γ_o} by $S_{\gamma_o}^{(5)}$, cf. section 4.

and (II-7.3), which give the first two terms of the expansion of D_s in correlations of *un*renormalized density fluctuations. Note however that the present expression for $D_s^{(2)}$ does not contain terms with factors $\underline{\underline{A}}_{\gamma_o}^{(m,m)}(\vec{r}=0)$, since these diagonal ring self-correlations are here already accounted for in the zeroth order term $D_s^{(0)}$, cf. the discussion in section 3. This is in contrast to the expansion given in ch. II, where corresponding factors did occur in the second order term (eq. (II-7.3)).

The above lowest order correction $D_s^{(2)}$ *may be evaluated using the* results of section 4 (cf. the similar calculation in ch. II, app. D). As in ch. II, we have restricted ourselves to a numerical evaluation of those terms in eq. (5.14) which do not contain connectors $\underline{\underline{A}}_{\gamma_o}^{(n,m)}$ with n or m larger than 2. This amounts to a restriction to corrections from monopole-dipole and dipole-dipole hydrodynamic interactions between density fluctuations. The results can be found in table 3.

Table 3

The $\delta\gamma$-expansion of D_s to second order

ϕ	$D_s^{(0)}/D_o$	+	$D_s^{(2)}/D_o$	=	D_s/D_o
0.05	0.887	+	0.012		0.90
0.10	0.781	+	0.012		0.79
0.15	0.685	+	0.007		0.69
0.20	0.598	-	0.000		0.60
0.25	0.521	-	0.008		0.51
0.30	0.454	-	0.014		0.44
0.35	0.397	-	0.020		0.38
0.40	0.348	-	0.023		0.33
0.45	0.307	-	0.025		0.28

6. Results and discussion

In the previous sections we have calculated the concentration dependence of the wavevector dependent (short-time) diffusion coefficient D(k) for spherical particles in suspension. For this purpose we derived the exact expression (5.2), from which one can obtain D(k) as an expansion in correlation functions of higher and higher order. The lowest order term in this expansion (eq. (5.5)) fully contains the many-body hydrodynamic interactions between an arbitrary number of spheres. Moreover, the contributions from a special class of correlations, the socalled (diagonal) ring self-correlations, are included in this term.

For the particular case of the (short-time) self-diffusion coefficient D_s (which is the large wavevector limit of D(k) and is given by eq. (3.11)) we were able to calculate not only the zeroth order term $D_s^{(0)}$ (eq. (5.12)), but also the lowest order correction $D_s^{(2)}$ thereto (eq. (5.14)), which is due to two-point correlations. In figure 1 we have plotted $D_s^{(0)}/D_o$ and $(D_s^{(0)}+D_s^{(2)})/D_o$ as a function of the volume fraction ϕ (from table 3). In the same figure we have also shown the corresponding results from the alternative expansion of D_s considered in ch. II: there the zeroth order term $D_s'^{(0)}$ contained no contributions due to correlations. If one compares the zeroth order results $D_s^{(0)}$ and $D_s'^{(0)}$ from these two alternative expansions (the two dotted curves in fig. 1), one sees that due to the inclusion of contributions from ring self-correlations the values for D_s in the absence of correlations decrease by almost 40% at the highest volume fractions. Moreover, the lowest order correction $D_s^{(2)}$ is in the present expansion at most 8% of $D_s^{(0)}$, whereas the corresponding term $D_s'^{(2)}$ in the expansion considered in ch. II was 20% of $D_s'^{(2)}$, at the highest volume fractions.

We conclude therefore, that the present expansion - resulting from an (algebraic) resummation of a special class of correlations - provides a more reliable zeroth order result for the diffusion coefficient than the expansion of ch. II. We note that to linear order in the density these two expansions are, however, identical*.

As argued in section 5, one may use an error estimate for D_s to obtain an indication of the accuracy of our lowest order result for

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*This results from the fact - observed in section 4 - that the renormalized density differs from the real density by terms of order ϕ^2.

D(k). Indeed $D_s/G(k)$ (where G(k) is the structure factor) gives at all wavevectors the largest contribution to D(k), which may also be written as (cf. eq. (5.11))

$$G(k)D(k) = D_s + k_B T N^{-1} \sum_{i\neq j} \langle \hat{k}\cdot\underline{\mu}_{ij}\cdot\hat{k}\, e^{i\vec{k}\cdot\vec{R}_{ij}}\rangle . \qquad (6.1)$$

To lowest order the r.h.s. of the above equation is given by eq. (5.5) and contains $D_s^{(0)}$ (cf. eq. (5.12)). It is found that adding the correction $D_s^{(2)}$ to $D_s^{(0)}$ changes this lowest order result for D(k) by less than 10% for wavevectors ak $\gtrsim$ 3 (where a is the radius of the suspended spheres). This remains the case for *all* values of the wavevector if the volume fraction ϕ does not exceed 0.3 . However, at small wavevectors and the highest densities considered, our lowest order results for D(k) become increasingly less accurate due to a near cancellation of the two terms on the r.h.s. of eq. (6.1).

In figs. 2 and 3 we have plotted for five values of the volume fraction ϕ the results* for $D(k)G(k)/D_0$ (which is the longitudinal part of the wavevector dependent sedimentation velocity, relative to its value at infinite dilution) and for $D_0/D(k)$. Note that in the absence of hydrodynamic interactions the first quantity is identically 1 and the second quantity equals the structure factor G(k). A comparison with experiments is possible for the large and small wavevector limits of D(k),

$$D_s = \lim_{k\to\infty} D(k),\quad D_c = \lim_{k\to 0} D(k), \qquad (6.2)$$

which are the (short-time) self and collective diffusion coefficients respectively. In fig. 4 we have plotted the theoretical values for these two coefficients, together with experimental results[3,7,8].

The diffusion coefficient at small wavevectors has been measured, by means of dynamic light-scattering, by Cebula, Ottewill, Ralston and

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*The values plotted contain the lowest order values calculated from eq. (5.5) to which the correction $D_s^{(2)}$ (given in table 3) has been added. In this way the values for D_s given in fig. 4 are obtained from figs. 2 and 3 in the limit k → ∞.

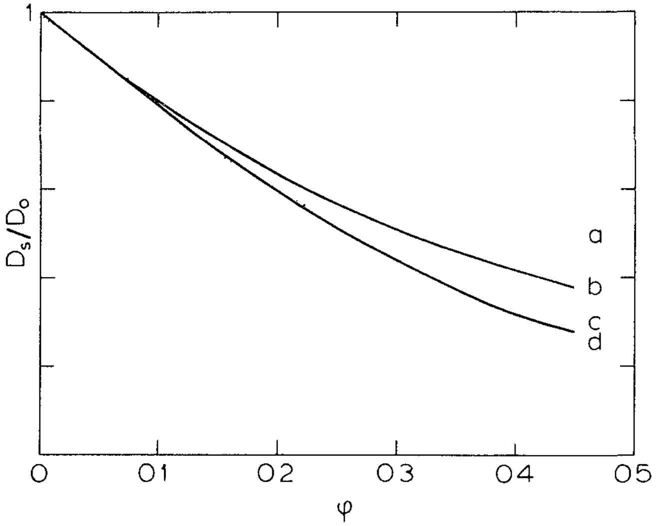

Fig. 1. D_s/D_o versus ϕ as results from the first two terms of the $\delta\gamma$-expansion considered here (curve c corresponding to $D_s^{(0)}$, curve d to $D_s^{(0)} + D_s^{(2)}$) and from the δn-expansion of ch. II (curve a: $D_s'^{(0)}$, curve b: $D_s'^{(0)} + D_s'^{(2)}$).

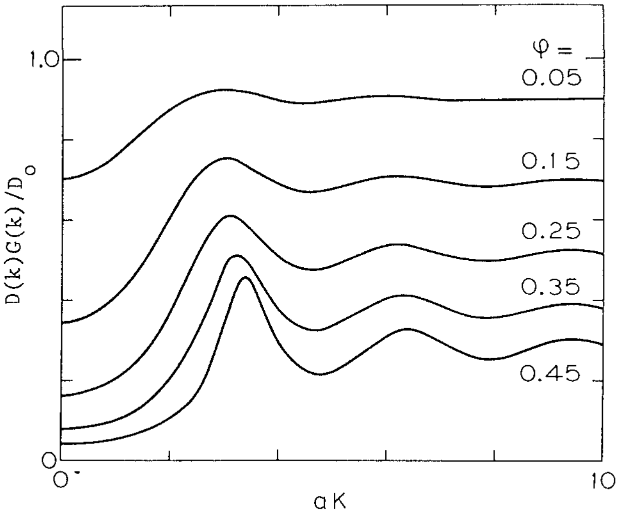

Fig. 2. Wavevector dependence of $D(k)G(k)/D_o$ for five values of ϕ.

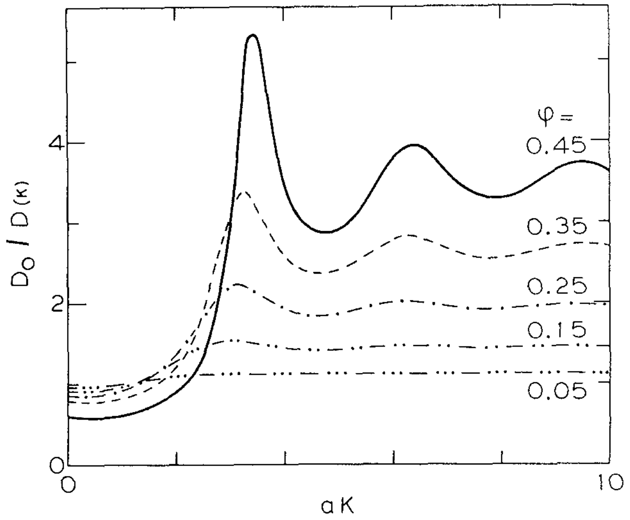

Fig. 3. Wavevector dependence of $D_0/D(k)$ for five values of ϕ.

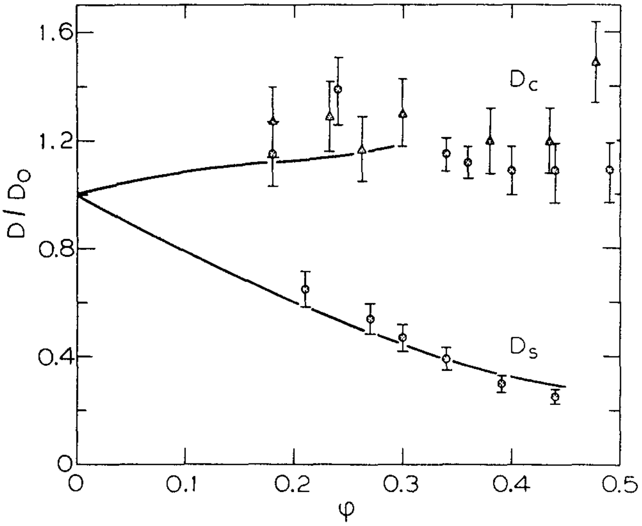

Fig. 4. ϕ-Dependence of the (short-time) self and collective diffusion coefficients, D_s/D_0 and D_c/D_0 respectively. The solid curves correspond to the values given in fig. 3, in the two limits of large and small wavevectors. Experimental data for D_s are taken from ref. 3 (lower dots), for D_c from refs. 7 (triangles) and 8 (upper dots).

Pusey[7] for micro-emulsion droplets and by Kops-Werkhoven and Fijnaut[8] for silica particles. These experiments both indicate that the collective diffusion coefficient is rather insensitive to changes in the concentration over a large range of volume fractions. This remarkable result is confirmed by our calculations of D_c, shown in fig. 4 for volume fractions $\phi \leqslant 0.3$ (as we remarked above, at higher concentrations our small wavevector results become less and less reliable due to cancellations). One should keep in mind, however, that on the time scale* of these experiments[7,8] a particle diffuses over a distance of several radii, whereas our results are - strictly speaking - valid only for short times in which the configuration of the particles remains essentially constant.

Pusey and van Megen[3] measured the diffusion coefficient of latex particles of radius $a = 0.6\ \mu$, at large wavevectors $k \approx 18/a$ for which $D(k)$ has attained its large-k limit. The time scale of these measurements is such that a particle diffuses over a distance of about a/10. For the densities considered one may therefore assume that the configuration of the particles is essentially constant on this time scale and that the measured quantity is indeed, as argued by Pusey and van Megen, the *short-time* self-diffusion coefficient. One sees from fig. 4 that the theoretical results for D_s agree with the measurements up to the highest volume fractions. We recall that in ch. II good agreement was obtained only for $\phi \lesssim 0.3$.

7. Interpretation in terms of an effective pair-mobility

Our lowest order result (5.5) for the diffusion coefficient can be written in a form similar to eq. (2.1)

$$D(k) = k_B T[NG(k)]^{-1} \sum_{i,j=1}^{N} \langle \hat{k} \cdot \underline{\mu}_{ij}^{eff} \cdot \hat{k}\, e^{i\vec{k}\cdot\vec{R}_{ij}} \rangle , \tag{7.1}$$

with $\underline{\mu}_{ij}^{eff}$ given by (cf. eqs. (5.8)-(5.10))

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*This time scale is the decay time of the electric field auto-correlation function, which is of the order of $(D_0 k^2)^{-1}$.

$$\underline{\mu}_{ij}^{eff} = (6\pi\eta a)^{-1}\,\frac{9}{2}\,(\frac{4}{3}\,\pi a^{3})(2\pi)^{-3}\int d\vec{k}\; e^{-i\vec{k}\cdot\vec{R}_{ij}}(\underline{1}-\hat{k}\hat{k})(ak)^{-4}\sin^{2}(ak)$$

$$\times\;[1+\phi S_{\gamma_o}(ak)]^{-1}. \qquad (7.2)$$

This quantity depends only on $\vec{R}_i$ and $\vec{R}_j$ and may therefore be interpreted as an *effective* pair-mobility. The renormalization factor $[1+\phi S_{\gamma_o}(ak)]^{-1}$ in this expression accounts for the many-body hydrodynamic interactions between an arbitrary number of spheres, including contributions from (diagonal) ring self-correlations.

For small values of ak, $S_{\gamma_o}(ak)$ behaves as

$$S_{\gamma_o}(ak) = \frac{5}{2}\,\gamma_o^{(2)}/n_o + O(ak)^2, \qquad (7.3)$$

as follows from expansion of definition (4.4). Since the largest contribution to the integral in eq. (7.2) arises from small values of ak, one may approximate $S_{\gamma_o}(ak)$ in the integrand by its small-k limit (the numerical consequences of this approximation for D(k) are discussed below). One then has for the effective pair-mobility the simple expression (cf. the evaluation of the connector $\underline{A}_{ij}^{(1,1)}$ in ref. 6)

$$\underline{\mu}^{eff} \approx (6\pi\eta^{*}a)^{-1}[\underline{1}\delta_{ij} + (1-\delta_{ij})(\tfrac{3}{4}(a/R_{ij})(\underline{1}+\hat{r}_{ij}\hat{r}_{ij}) +$$

$$+\;\tfrac{1}{2}(a/R_{ij})^{3}(\underline{1}-3\hat{r}_{ij}\hat{r}_{ij}))], \qquad (7.4)$$

with the definition

$$\eta^{*} \equiv \eta(1+\frac{5}{2}\,\phi\gamma_o^{(2)}/n_o). \qquad (7.5)$$

The vector $\vec{R}_{ij} \equiv \vec{R}_j - \vec{R}_i$ has magnitude R_{ij} and direction $\hat{r}_{ij} \equiv \vec{R}_{ij}/R_{ij}$. The renormalized density $\gamma_o^{(2)}$ is given as a function of n_o in table 1.

If one calculates D(k) from eq. (7.1), with the approximation (7.4) (using the Percus-Yevick pair correlation function), one finds values for D(k) which are smaller than the results[†] shown in fig. 3, espe-

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[†] We recall that these values result from eqs. (7.1) and (7.2), with the addition of the correction $D_s^{(2)}/G(k)$, from table 3.

cially at small wavevectors. For ak $\gtrsim 3$, however, the difference is less than 10%, over the whole range of volume fractions. For self-diffusion in particular, one finds from eq. (7.4) that (cf. eq. (2.2))

$$D_s \approx k_B T(6\pi\eta^* a)^{-1}. \tag{7.6}$$

This formula differs from our full result (fig. 4) by at most 7%.

Expression (7.4) for the effective pair-mobility has a simple physical interpretation: it is the mobility tensor - up to terms of order $(a/R_{ij})^4$ - of two spheres, in a fluid with viscosity η^*. We shall show in the next chapter that, within the order of approximation of eq. (7.1), η^* equals the effective viscosity of the suspension. To linear order in the density this identification is in fact exact, since $\gamma_o^{(2)} = n_o + O(\phi^2)$ (cf. remark after eq. (4.9)), so that

$$\eta^* = \eta\left(1 + \frac{5}{2}\phi + O(\phi^2)\right), \tag{7.7}$$

which is Einstein's result for the effective viscosity.

We stress the fact (noted also in ch. II) that the hydrodynamic interaction between two particles in a suspension is *not screened* by the presence of the other particles. By this we mean that the effective pair-mobility discussed above is of long range (it falls off as 1/R). In contrast, Snook, van Megen and Tough[10] have proposed an empirical *screened* pair-mobility to reproduce the experimental data for the diffusion coefficient. In view of the above, there does not appear to be a physical motivation for their choice.

It should be mentioned that screening of hydrodynamic interactions does occur in a different system, viz. in a porous medium consisting of *immobile* particles in a viscous fluid (see e.g. ref. 11). The properties of such a medium - which are different from those of a suspension, in which the particles may move freely - were studied (in particular for large concentrations of the particles) by Muthukumar[12], including also the effect of many-body hydrodynamic interactions.

Appendix. Proof of eq. (3.7)

We start from the identity

$$\mathcal{A}(1-n\,\underset{\sim}{\mathcal{Q}}\mathcal{B}^{-1}\mathcal{A}\,)^{-1}n = \mathcal{A}_{\gamma_0}[\mathit{1} - (n-\gamma_0)\,\underset{\sim}{\mathcal{Q}}\mathcal{B}^{-1}\,\mathcal{A}_{\gamma_0}]^{-1}n, \qquad (A.1)$$

where $\mathcal{A}_{\gamma_0}$ has been defined in eq. (3.2). It is convenient to define an operator I with kernel

$$I(\vec{r}\,|\,\vec{r}\,') = \begin{cases} 1, \text{ if } \vec{r} = \vec{r}\,', \\ 0, \text{ if } \vec{r} \neq \vec{r}\,', \end{cases} \qquad (A.2)$$

and a matrix $\mathcal{B}_{\gamma_0}$ with elements

$$\{\,\mathcal{B}_{\gamma_0}\}_{n,m} = \delta_{nm}\,\underline{A}_{\gamma_0}^{(m,m)}\,(\vec{r}=0). \qquad (A.3)$$

With these notations we can write

$$\mathcal{A}_{\gamma_0} = \overset{\circ}{\mathcal{A}}_{\gamma_0} + \mathcal{B}_{\gamma_0}\,I, \qquad (A.4)$$

where $\overset{\circ}{\mathcal{A}}_{\gamma_0}$ is defined in eq. (3.8). In the same compact notation we have for $\gamma \equiv \gamma_0 n_0^{-1}\; n$,

$$\gamma = n(\mathit{1} - \,\underset{\sim}{\mathcal{Q}}\mathcal{B}^{-1}\,\mathcal{B}_{\gamma_0}\,)^{-1}, \qquad (A.5)$$

cf. eqs. (3.1) and (3.3).

We note that as a consequence of the fact that $\mathcal{A}_{\gamma_0} I = 0$, one has the identity

$$\mathcal{A}_{\gamma_0} = \mathcal{A}_{\gamma_0}(\mathit{1} - \gamma_0\,\underset{\sim}{\mathcal{Q}}\mathcal{B}^{-1}\,\mathcal{B}_{\gamma_0}\,I)^{-1}. \qquad (A.6)$$

Upon substitution into the r.h.s. of eq. (A.1) and repeated use of definition (A.4) one then finds

$$A(1 - n\,\mathcal{Q}\mathcal{B}^{-1} A)^{-1} n = A_{\gamma_o}\left(1 - n\,\mathcal{Q}\mathcal{B}^{-1} A_{\gamma_o} + \gamma_o\,\mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{A}_{\gamma_o}\right)^{-1} n =$$

$$= A_{\gamma_o}\left(1 - (1 - n\,\mathcal{Q}\mathcal{B}^{-1} \mathcal{B}_{\gamma_o} I)^{-1} (n - \gamma_o)\,\mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{A}_{\gamma_o}\right)^{-1} (1 - n\,\mathcal{Q}\mathcal{B}^{-1} \mathcal{B}_{\gamma_o} I)^{-1} n. \qquad (A.7)$$

We now use the identity

$$(1 - n\,\mathcal{Q}\mathcal{B}^{-1} \mathcal{B}_{\gamma_o} I)^{-1} \gamma_o\,\mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{A}_{\gamma_o} = \gamma_o\,\mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{A}_{\gamma_o}, \qquad (A.8)$$

which follows from $I \overset{\circ}{A}_{\gamma_o} = 0$, and another identity

$$(1 - n\,\mathcal{Q}\mathcal{B}^{-1} \mathcal{B}_{\gamma_o} I)^{-1} n = n(1 - \mathcal{Q}\mathcal{B}^{-1} \mathcal{B}_{\gamma_o})^{-1} \equiv \gamma, \qquad (A.9)$$

(cf. eq. (A.5)). Eq. (A.9) is a consequence of the fact that $nIn = n$. Substituting eqs. (A.8) and (A.9) into eq. (A.7), one then finds

$$A(1 - n\,\mathcal{Q}\mathcal{B}^{-1} A)^{-1} n = A_{\gamma_o}(1 - \delta\gamma\,\mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{A}_{\gamma_o})^{-1} \gamma, \qquad (A.10)$$

where $\delta\gamma \equiv \gamma - \gamma_o$. This is the required formula (3.7).

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CHAPTER IV

EFFECTIVE VISCOSITY

1. Introduction

The concentration dependence of the effective viscosity η^{eff} of a suspension of spherical particles in a fluid (with viscosity η_o) is well understood in the regime of low concentrations. To second order in the volume fraction ϕ of the suspended particles one has the expansion

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\phi + 5.2\phi^2. \tag{1.1}$$

The coefficient of the linear term was first calculated by Einstein[1] (cf. also ref. 2); the quadratic term has been evaluated by several authors[3-7], the value given in eq. (1.1) being due to Batchelor and Green[4] (with an error-estimate of 6%)*.

Up to the order given in eq. (1.1) it is sufficient to consider only the hydrodynamic interactions between pairs of particles. Higher order terms, however, contain contributions from specific hydrodynamic interactions of three and more spheres. In fact it has been demonstrated in ch. II in the context of diffusion that these many-sphere hydrodynamic interactions may not be neglected if the suspension is not dilute.

In order to simplify the problem of solving the hydrodynamic equa-

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*Contributions to the effective viscosity from Brownian motion of the spheres are neglected in these analyses, as well as in the present investigation. We shall return to this point in section 8.

tions of motion in the presence of more than two spheres, an approximation which neglects the finite size of the spheres is customary. Several authors[8-10], for example, have treated the suspension as a mixture of two fluids, one fluid (with volume fraction ϕ) having an infinitely large viscosity, the other fluid having viscosity η_o. This approach yields a very simple formula for the effective viscosity*

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi(1 - \frac{5}{2}\,\phi)^{-1}, \tag{1.2}$$

which for small ϕ is in good agreement with eq. (1.1). Indeed, one might expect that a point-particle approximation is reasonable if the suspension is sufficiently dilute, since in that case the average distance between the spheres is large compared to their radius. At higher concentrations, however, this approximation is unjustified and leads to incorrect results, as we shall see in this chapter.

In this chapter we present a theory for the effective viscosity which *fully* accounts for the hydrodynamic interactions between an arbitrary number of spheres. Our analysis is based on: i) a general scheme, developed by Mazur and van Saarloos[12], to solve the hydrodynamic many-sphere interaction problem; ii) a technique of calculating the influence of many-sphere hydrodynamic interactions on transport properties of suspensions, by means of an expansion in correlation functions of fluctuations in the concentration of the spheres of higher and higher order. Such an expansion has been used in the previous chapter in the context of diffusion.

In section 2 we give a formal theory for the wavevector dependent effective viscosity $\eta(k)$ (of which the quantity η^{eff} considered above is the zero-wavevector limit) of a suspension of spheres, by considering the average response of the suspension to an externally applied force. This theory (which makes essential use of the socalled method of induced forces[13,14]) differs from the conventional approach where the dependence of stress on shear is considered. To obtain the effective viscosity by this second method (used e.g. by Peterson and

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*This same formula was first derived by Lundgren[11], from a different starting point.

Fixman[3]), one must find both the average stress and gradient of the average flow velocity and eliminate the imposed flow between these quantities. This double calculation is not necessary in the first method (used e.g. by Freed and Muthukumar[7]), where one finds the effective viscosity directly from the dependence of the average flow velocity on the external force.

Using results for many-sphere hydrodynamic interactions obtained by Mazur and van Saarloos[12] (cf. section 3), we find in this way in section 4 an explicit expression for the effective viscosity $\eta(k)$. As illustrated in section 5, a calculation of coefficients in the expansion of this quantity in powers of the concentration is from this point on straightforward. (The zero-wavevector results given in this section were previously obtained by Freed and Muthukumar[7] by a similar method, cf. the preceding paragraph.)

If the suspension is not dilute, an expansion in the concentration is no longer appropriate. For this reason we study in sections 6 and 7 the effective viscosity of a concentrated suspension through an expansion in density-fluctuation correlation functions of increasing order, along the lines of ch. III. Each term in this expansion accounts for the hydrodynamic interactions of an arbitrary number of spheres, and contains the resummed contributions from a class of self-correlations. Results for the wavevector and concentration dependence of $\eta(k)$ are given in fig. 1 and table 1. In section 8 we discuss these results and give a comparison with previous work and experimental data. It is found, in particular, that the divergency of the effective viscosity which follows from the point-particle approximation (cf. eq. (1.2)) does not occur if the finite size of the spheres is accounted for properly.

We conclude in section 9 with a discussion of the relation between effective viscosity of a suspension and diffusion coefficient of the suspended spheres. In particular, we show that - within a certain approximation - the product of η^{eff} and self-diffusion coefficient is independent of the concentration.

2. Formal theory for the effective viscosity

We consider a suspension of N spherical particles with radius a in an incompressible fluid with viscosity η_o. We describe the motion of the fluid by the quasi-static Stokes equation, which - within the context of the method of induced forces[13,14] - reads

$$\vec{\nabla}p(\vec{r}) - \eta_o\Delta\vec{v}(\vec{r}) = \vec{F}^{ext}(\vec{r}) + \sum_{j=1}^{N} \vec{F}_j^{ind}(\vec{r}), \tag{2.1}$$

$$\vec{\nabla}\cdot\vec{v}(\vec{r}) = 0. \tag{2.1a}$$

Here $\vec{v}(\vec{r})$ is the velocity field, $p(\vec{r})$ the hydrostatic pressure and $\vec{F}^{ext}(\vec{r})$ an external force density. The induced force densities $\vec{F}_j^{ind}(\vec{r})$ (j = 1,2,...N) are to be chosen in such a way that

$$\vec{F}_j^{ind}(\vec{r}) = 0 \qquad \text{for } |\vec{r} - \vec{R}_j| > a, \tag{2.2}$$

$$\vec{v}(\vec{r}) = \vec{u}_j + \vec{\omega}_j \wedge(\vec{r} - \vec{R}_j) \qquad \text{for } |\vec{r} - \vec{R}_j| \leqslant a, \tag{2.3}$$

$$p(\vec{r}) = 0 \qquad \text{for } |\vec{r} - \vec{R}_j| < a, \tag{2.3a}$$

so that the velocity of the fluid satisfies stick boundary conditions on the surfaces of the spheres. In these equations $\vec{R}_j$ is the position vector of the center of sphere j, and $\vec{u}_j$ and $\vec{\omega}_j$ are its velocity and angular velocity respectively. We shall assume that the spheres move freely in a large volume V, so that the forces and torques on the spheres are zero. From eqs. (2.1) and (2.2) one therefore finds for the force density induced on each sphere

$$\int d\vec{r}\, \vec{F}_j^{ind}(\vec{r}) = 0, \int d\vec{r}\, (\vec{r} - \vec{R}_j) \wedge \vec{F}_j^{ind}(\vec{r}) = 0, \tag{2.4}$$

(where we have furthermore assumed that $\vec{F}^{ext}(\vec{r})$ is non-zero outside V only).

In order to obtain a formal solution of eq. (2.1) it is convenient to introduce the Fourier transform of $\vec{v}(\vec{r})$,

$$\vec{v}(\vec{k}) = \int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}}\, \vec{v}(\vec{r}), \tag{2.5}$$

and similarly of $p(\vec{r})$ and $\vec{F}^{ext}(\vec{r})$. The Fourier transform of $\vec{F}_j^{ind}(\vec{r})$ is defined (for each j) in a reference frame in which sphere j is at the origin

$$\vec{F}_j^{ind}(\vec{k}) = \int d\vec{r}\; e^{-i\vec{k}\cdot(\vec{r}-\vec{R}_j)}\, \vec{F}_j^{ind}(\vec{r}). \tag{2.6}$$

The formal solution of eq. (2.1) is then found to be

$$\vec{v}(\vec{k}) = \left(\eta_o k^2\right)^{-1}(\underline{1} - \hat{k}\hat{k})\cdot[\vec{F}^{ext}(\vec{k}) + \sum_{j=1}^{N} e^{-i\vec{k}\cdot\vec{R}_j}\, \vec{F}_j^{ind}(\vec{k})]. \tag{2.7}$$

(The wavevector $\vec{k}$ has magnitude k and direction $\hat{k} \equiv \vec{k}/k$; $\underline{1}$ denotes the second rank unit tensor.)

Following the general scheme of Mazur and van Saarloos[12], one can use eqs. (2.2)-(2.4) to eliminate the induced forces in eq. (2.7) in favor of the external force. The resulting solution for the velocity field is of the form

$$\vec{v}(\vec{r}) = \int d\vec{r}\,'\; \underline{M}(\vec{r}\,|\vec{r}\,')\cdot\vec{F}^{ext}(\vec{r}\,'). \tag{2.8}$$

An explicit expression for the tensor $\underline{M}(\vec{r}\,|\vec{r}\,')$ is derived in appendix A. The macroscopic velocity field may now be obtained by averaging eq. (2.8) over the equilibrium distribution function of the positions of the N spheres in the volume V. For an infinite system the average $\langle\underline{M}(\vec{r}\,|\vec{r}\,')\rangle$ will depend on the separation $\vec{r}\,'- \vec{r}$ only, as a consequence of translational invariance of the distribution function. In view of incompressibility of the fluid (eq. (2.1a)), this average must be of the form

$$\langle\underline{M}(\vec{r}\,|\vec{r}\,')\rangle = (2\pi)^{-3} \int d\vec{k}\; e^{-i\vec{k}\cdot(\vec{r}\,'- \vec{r})}\left(\eta(k)k^2\right)^{-1}(\underline{1} - \hat{k}\hat{k}), \tag{2.9}$$

giving for the macroscopic velocity the expression

$$\langle\vec{v}(\vec{k})\rangle = \left(\eta(k)k^2\right)^{-1}(\underline{1} - \hat{k}\hat{k})\cdot\vec{F}^{ext}(\vec{k}). \tag{2.10}$$

The function $\eta(k)$ defined through eq. (2.9) represents the wavevector dependent *effective* viscosity of the suspension: indeed eq. (2.10) gives the velocity field due to an external force $\vec{F}^{ext}(\vec{k})$ in an incompressible fluid with viscosity $\eta(k)$.

3. Results from the hydrodynamic analysis

As we show in appendix A, the tensor $\underline{M}(\vec{r}|\vec{r}\,')$ - which relates the velocity at point $\vec{r}$ to the external force density at point $\vec{r}\,'$ (eq. (2.8)) - may straightforwardly be derived from the results of Mazur and van Saarloos[12]. One finds the expression

$$6\pi\eta_0 a\,\underline{M}(\vec{r}|\vec{r}\,') = \underline{T}^{(1,1)}(\vec{r}\,'-\vec{r}) + \sum_{n,m=2}^{\infty}\sum_{i,j=1}^{N}\underline{T}^{(1,n)}(\vec{R}_i-\vec{r})\odot\underline{\zeta}_{ij}^{(n,m)}\odot\underline{T}^{(m,1)}(\vec{r}\,'-\vec{R}_j), \qquad (3.1)$$

where $\underline{\zeta}_{ij}^{(n,m)}$ is given as an infinite series of reflections or scatterings from the spheres,

$$\underline{\zeta}_{ij}^{(n,m)} = \underline{B}^{(n,n)^{-1}}\delta_{nm}\delta_{ij} + \underline{B}^{(n,n)^{-1}}\odot\underline{A}_{ij}^{(n,m)}\odot\underline{B}^{(m,m)^{-1}}(1-\delta_{ij})$$

$$+\sum_{s=1}^{\infty}\sum_{p_1=2}^{\infty}\sum_{p_2=2}^{\infty}\cdots\sum_{p_s=2}^{\infty}\;\sum_{\substack{j_1=1\\ j_1\neq i}}^{N}\;\sum_{\substack{j_2=1\\ j_2\neq j_1}}^{N}\cdots\sum_{\substack{j_s=1\\ j_s\neq j_{s-1},j}}^{N}\underline{B}^{(n,n)^{-1}}\odot\underline{A}_{ij_1}^{(n,p_1)}$$

$$\odot\,\underline{B}^{(p_1,p_1)^{-1}}\odot\underline{A}_{j_1j_2}^{(p_1,p_2)}\odot\ldots\underline{B}^{(p_s,p_s)^{-1}}\odot\underline{A}_{j_sj}^{(p_s,m)}\odot\underline{B}^{(m,m)^{-1}}\;. \qquad (3.2)$$

The objects $\underline{\zeta}_{ij}^{(n,m)}$, $\underline{T}^{(n,m)}(\vec{r})$, $\underline{A}_{ij}^{(n,m)}$ and $\underline{B}^{(n,m)^{-1}}$ in the above equations are tensors of rank n+m. The dot $\odot$ in e.g. $\underline{A}_{ij}^{(n,m)}\odot\underline{B}^{(m,m)^{-1}}$ prescribes an m-fold contraction, with the (nesting) convention that the last index of the first tensor is contracted with the first index of the second tensor, etc. The definitions of the tensors $\underline{T}$, $\underline{A}$ and

$\underline{B}^{-1}$ will be given below.

We first notice that in the absence of suspended particles only the first of the terms on the r.h.s. of eq. (3.1) remains, which is the wellknown Oseen tensor (see below). The perturbation of the fluid flow by the spheres is accounted for by the generalized (dimensionless) friction tensors $\underline{\zeta}_{ij}^{(n,m)}$, which relate an n-th order multipole moment of the induced force on sphere i to an m-th order multipole moment of the unperturbed flow on the surface of sphere j (cf. eq. (A.4) in appendix A). If there is just one sphere, $\underline{\zeta}_{ii}^{(n,m)}$ is unequal to zero only for n=m and different multipole moments are uncoupled. The hydrodynamic interactions between two and more spheres are given by the series of products of tensors $\underline{A}$ and $\underline{B}^{-1}$ in eq. (3.2). This series constitutes an expansion in inverse powers of the interparticle separation, in view of the following property[12] of the "connectors" $\underline{A}_{ij}^{(n,m)}$ (defined for i≠j)

$$\underline{A}_{ij}^{(n,m)} = \underline{G}_{ij}^{(n,m)} R_{ij}^{-(n+m-1)} + \underline{F}_{ij}^{(n,m)} R_{ij}^{-(n+m+1)} , \tag{3.3}$$

where the tensors $\underline{G}_{ij}$ and $\underline{F}_{ij}$ depend only on the direction of the vector $\vec{R}_{ij} \equiv \vec{R}_j - \vec{R}_i$ (and not on its magnitude R_{ij}). The tensor $\underline{B}^{-1}$, on the other hand, is independent of the positions of the spheres.

We shall now give the definitions of the tensors occuring in eqs. (3.1) and (3.2). The general expression for the connectors $\underline{A}_{ij}^{(n,m)}$ in terms of the connector field $\underline{A}^{(n,m)}(\vec{r})$ is given in eqs. (II-2.3), (II-2.4), (II-2.14) and (II-2.15). The "propagator" $\underline{T}^{(n,m)}(\vec{r})$ is defined in terms of its Fourier transform by

$$\underline{T}^{(n,m)}(\vec{k}) \equiv \int d\vec{r}\; e^{i\vec{k}\cdot\vec{r}}\, \underline{T}^{(n,m)}(\vec{r}) = 6\pi a i^{n-m}(2n-1)!!(2m-1)!! \\ \times k^{-2} j'_{n-1}(ak) j'_{m-1}(ak)\, \overline{\hat{k}^{n-1}}\, (\underline{1} - \hat{k}\hat{k})\, \overline{\hat{k}^{m-1}} , \tag{3.4}$$

with the definition

$$j'_p(x) = j_p(x) \quad \text{for } p\geq 1, \; j'_0(x) \equiv 1, \tag{3.5}$$

where $j_p(x) \equiv (\frac{1}{2}\pi/x)^{\frac{1}{2}} J_{p+\frac{1}{2}}(x)$ is a spherical Bessel function. Finally we recall that expressions for the constant tensors $\underline{B}^{(n,n)^{-1}}$ $(n \geqslant 2)$ are given in eqs. (II-2.6) and (II-2.22).

4. Formulae for the effective viscosity

We shall in this section combine the results from the previous two sections to give explicit formulae for the effective viscosity. We first note that, according to eq. (3.1), the Fourier transform

$$\underline{M}(\vec{k}|\vec{k}') = \int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}} \int d\vec{r}'\; e^{i\vec{k}'\cdot\vec{r}'}\, \underline{M}(\vec{r}|\vec{r}') \tag{4.1}$$

of the kernel $\underline{M}(\vec{r}|\vec{r}')$ is given by

$$6\pi\eta_o a\, \underline{M}(\vec{k}|\vec{k}') = (2\pi)^3 \delta(\vec{k}' - \vec{k})\, \underline{T}^{(1,1)}(\vec{k}) + \sum_{n,m=2}^{\infty} \sum_{i,j=1}^{N} \underline{T}^{(1,n)}(\vec{k}) \odot e^{-i\vec{k}\cdot\vec{R}_i}\, \underline{\zeta}_{ij}^{(n,m)}\, e^{i\vec{k}'\cdot\vec{R}_j} \odot \underline{T}^{(m,1)}(\vec{k}'). \tag{4.2}$$

From translational invariance of $\underline{\zeta}_{ij}$ and of the distribution function it follows that (for an infinite system)

$$\langle \sum_{i,j=1}^{N} e^{-i\vec{k}\cdot\vec{R}_i}\, \underline{\zeta}_{ij}^{(n,m)}\, e^{i\vec{k}'\cdot\vec{R}_j} \rangle = n_o (2\pi)^3 \delta(\vec{k}'-\vec{k}) \times \langle N^{-1} \sum_{i,j=1}^{N} \underline{\zeta}_{ij}^{(n,m)}\, e^{i\vec{k}\cdot\vec{R}_{ij}} \rangle, \tag{4.3}$$

where $n_o = N/V$ is the average number density of the particles.

From eqs. (2.9) and (4.2) we then find, with the help of eq. (4.3), for the wavevector dependent effective viscosity $\eta(k)$ the formula

$$6\pi a \big(\eta_o/\eta(k) - 1\big)(\underline{1} - \hat{k}\hat{k}) = n_o k^2 \sum_{n,m=2}^{\infty} \underline{T}^{(1,n)}(\vec{k}) \odot \langle N^{-1} \sum_{i,j=1}^{N} \underline{\zeta}_{ij}^{(n,m)}\, e^{i\vec{k}\cdot\vec{R}_{ij}} \rangle \odot \underline{T}^{(m,1)}(\vec{k}). \tag{4.4}$$

Use has also been made here of the explicit expression for $\underline{T}^{(1,1)}(\vec{k})$ (eq. (3.4)). One may verify (using the fact that $\vec{k}\cdot\underline{T}^{(1,n)}(\vec{k}) = 0$ for all n, cf. eq. (3.4)) that the r.h.s. of eq. (4.4) is the product of a scalar function of k and the tensor $\underline{1} - \hat{k}\hat{k}$, as implied by the l.h.s. of this equation.

At infinite dilution the r.h.s. of eq. (4.4) vanishes and $\eta(k)$ equals η_o for all k, as it should. The influence of the suspended particles on the viscosity of the suspension is taken into account by the term on the r.h.s. of eq. (4.4), to *all* orders in their concentration. We observe that this term vanishes in the limit $k\to\infty$ (cf. eq. (3.8)), so that in this limit the effective viscosity is equal to the viscosity of the fluid

$$\lim_{k\to\infty} \eta(k) = \eta_o. \tag{4.5}$$

This limiting behaviour reflects the fact that for large wavevectors the Fourier transformed imposed velocity field of the fluid remains almost unperturbed by the presence of the spheres.

The zero-wavevector limit of the effective viscosity is of particular interest in the study of properties of suspensions. We denote this quantity by

$$\eta^{eff} \equiv \lim_{k\to 0} \eta(k). \tag{4.6}$$

From the fact that $\underline{T}^{(r,s)}(\vec{k})$ is of order k^{r+s-4} for small k (cf. eq. (3.4)) it follows that only the term with n=m=2 in the series on the r.h.s. of eq. (4.4) gives a non-vanishing contribution in the limit $k\to 0$. For η^{eff} we therefore have the more simple formula

$$(\eta_o /\eta^{eff} - 1)(\underline{1} - \hat{k}\hat{k}) = \lim_{\varepsilon\to 0} \frac{9}{2}\, \phi(\underline{1} - \hat{k}\hat{k})\hat{k}:\langle N^{-1} \sum_{i,j=1}^{N} \underline{\zeta}_{ij}^{(2,2)}\, e^{i\varepsilon\hat{k}\cdot\vec{R}_{ij}}\rangle$$
$$:\hat{k}(\underline{1} - \hat{k}\hat{k}), \tag{4.7}$$

where the colon indicates a double contraction and ϕ denotes the volume fraction of the spheres.

Eqs. (4.4) and (4.7) are a most convenient starting point for the calculation of the (wavevector dependent) effective viscosity of a suspension, by means of an expansion in powers of the concentration of the suspended particles. This will be illustrated in the next section. In order to study also the behaviour of the effective viscosity at high concentrations (where such an expansion is no longer appropriate) we shall now cast eq. (4.4) in a different form - adopting an operator notation which has proved its use in the previous chapters.

First we define a modified connector field $\underline{\tilde{A}}^{(n,m)}(\vec{r})$ and a convolution operator $\underline{\tilde{A}}^{(n,m)}$ as in eqs. (II-3.4) and (II-3.10). Similarly, we define an operator $\underline{T}^{(n,m)}$ with kernel

$$\underline{T}^{(n,m)}(\vec{r}|\vec{r}\,') = \underline{T}^{(n,m)}(\vec{r}\,'- \vec{r}). \tag{4.8}$$

Next we introduce a matrix $\mathcal{H}$ of which these operators are the elements

$$\{\mathcal{H}\}_{n,m} = \begin{cases} \underline{T}^{(n,m)} & \text{if } n=1 \text{ or } m=1, \\ \underline{\tilde{A}}^{(n,m)} & \text{if } n\neq 1 \text{ and } m\neq 1. \end{cases} \tag{4.9}$$

and matrices $\mathcal{B}^{-1}$ and $\mathcal{Q}$ as in eqs. (II-3.12) and (II-3.13). Finally, we recall the definition of the diagonal operator n, which corresponds to the microscopic density field $n(\vec{r})$, in eqs. (II-3.7) and (II-3.9).

For the kernel $\underline{M}(\vec{r}|\vec{r}\,')$, given by eqs. (3.1) and (3.2), we now have in this compact notation

$$6\pi\eta_0 a\, \underline{M}(\vec{r}|\vec{r}\,') = \{\mathcal{H}(\mathcal{1} - n\mathcal{Q}\mathcal{B}^{-1}\mathcal{H})^{-1}\}_{1,1}(\vec{r}|\vec{r}\,'). \tag{4.10}$$

In this equation the kernel is taken of the 1,1 element of the matrix of operators between braces. From eqs. (2.9) and (4.10) we thus find for the effective viscosity $\eta(k)$ the operator formula

$$\frac{1}{\eta(k)}\{\mathcal{H}\}_{1,1}(\vec{k}|\vec{k}\,') = \frac{1}{\eta_0}\langle\{\mathcal{H}(\mathcal{1} - n\mathcal{Q}\mathcal{B}^{-1}\mathcal{H})^{-1}\}_{1,1}(\vec{k}|\vec{k}\,')\rangle, \tag{4.11}$$

where the Fourier transform of an operator kernel was defined in eq.

(4.1). This alternative formula is a convenient starting point for the calculation of the effective viscosity of a concentrated suspension, by means of an expansion in density-fluctuation correlation functions of higher and higher order, cf. section 6.

5. Expansion in powers of the concentration

At low concentrations of the suspended particles an expansion of the effective viscosity in powers of the concentration is appropriate.

To *first* order in the concentration eqs. (3.2) and (4.4) give

$$6\pi a\left(\eta_o/\eta(k) - 1\right)(\underline{1} - \hat{k}\hat{k}) = n_o k^2 \sum_{m=2}^{\infty} \underline{T}^{(1,m)}(\vec{k}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{T}^{(m,1)}(\vec{k}). \qquad (5.1)$$

The series in this equation may be summed analytically, in precisely the same way as the corresponding series for the connector field $\underline{A}$ was summed in eq. (II-6.5). The result is

$$\left(\eta_o/\eta(k) - 1\right)(\underline{1} - \hat{k}\hat{k}) = - \phi S(ak)(\underline{1} - \hat{k}\hat{k}), \qquad (5.2)$$

where the function S(x) is defined in eq. (II-6.6). Eq. (5.2) implies

$$\eta(k) = \eta_o[1 + \phi S(ak) + \mathcal{O}(\phi^2)], \qquad (5.3)$$

representing an extension of Einstein's[1,2] formula for the effective viscosity at zero wavevector to arbitrary values of k. For small k, the function S(ak) behaves as

$$S(ak) = \frac{5}{2} - \frac{3}{350}(ak)^4 + \mathcal{O}(ak)^6, \qquad (5.4)$$

as follows from expansion of the r.h.s. of eq. (II-6.6). It is noteworthy that the term of order $(ak)^2$ does not occur in this expansion, and that hence the finite wavevector corrections to Einstein's formula are of *fourth* order. Bedeaux, Kapral and Mazur[5], on the contrary, found a nonzero coefficient for the term of order $\phi(ak)^2$ in the effective viscosity. It has been pointed out by Schmitz[6,15], however, that eq. (4.7) in the paper by Bedeaux et al. (which gives the function which relates the symmetric gradient of the velocity field perturbed by the presence of one sphere to the symmetric gradient of the unperturbed field) is incorrect as far as terms of second power in the wavevector are concerned. Indeed an error in this order would affect the value of the coefficient mentioned above.

To *second* order in the concentration, only those terms in expression (3.2) for the generalized friction tensors contribute to the effective viscosity, which depend on the positions of at most two spheres. For the dipole-dipole friction tensor $\underline{\zeta}_{ij}^{(2,2)}$ we find, restricting ourselves to these terms, (cf. also eqs. (3.3) and (II-2.6))

$$\underline{\zeta}_{ij}^{(2,2)} = -\frac{10}{9}\,\delta_{ij}\,\underline{\Delta} + \left(-\frac{10}{9}\right)^2 (1-\delta_{ij})\,\underline{A}_{ij}^{(2s,2s)}$$

$$+\left(-\frac{10}{9}\right)^3 \delta_{ij} \sum_{k\neq i} R_{ik}^{-6}\,\underline{G}_{ik}^{(2s,2s)} : \underline{G}_{ki}^{(2s,2s)} + \mathcal{O}(R^{-8}), \qquad (5.5)$$

to eighth order* in the expansion in inverse powers of the separation of the spheres R. (The tensor $\underline{\Delta}$ used in this equation is identical to the tensor $\underline{\Delta}^{(2,2)}$ defined in eq. (II-2.10).) The connector $\underline{A}^{(2s,2s)} \equiv \underline{\Delta} : \underline{A}^{(2,2)} : \underline{\Delta}$ is traceless and symmetric in both the first and second pair of indices; it consists of two terms of order R^{-3} and R^{-5} respectively (cf. eq. (3.3)). The tensor $\underline{G}_{ik}^{(2s,2s)}$ is given by[12]

$$\underline{G}_{ik}^{(2s,2s)} = -\frac{9}{4}\,a^3\,\underline{\Delta} : (5\hat{r}_{ik}\hat{r}_{ik}\hat{r}_{ik}\hat{r}_{ik} - 2\hat{r}_{ik}\,\underline{1}\,\hat{r}_{ik}) : \underline{\Delta}, \qquad (5.6)$$

where $\hat{r}_{ik} \equiv \vec{R}_{ik}/R_{ik}$ is the unit vector in the direction of $\vec{R}_{ik}$. From this last equation one readily finds

$$\left(-\frac{10}{9}\right)^3 R_{ik}^{-6}\,\underline{G}_{ik}^{(2s,2s)} : \underline{G}_{ki}^{(2s,2s)} = -\frac{125}{9}\left(\frac{a}{R_{ik}}\right)^6 \underline{\Delta} : (2\hat{r}_{ik}\hat{r}_{ik}\hat{r}_{ik}\hat{r}_{ik}$$

$$+\,\hat{r}_{ik}\,\underline{1}\,\hat{r}_{ik}) : \underline{\Delta}. \qquad (5.7)$$

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*The absence of a term of order R^{-7} in the expansion of $\underline{\zeta}_{ij}^{(2,2)}$ in powers of 1/R is noteworthy.

The above equations enable us to calculate the zero wavevector limit η^{eff} of the effective viscosity to second order in the concentration. Substituting eq. (5.5) into formula (4.7) one finds for this quantity the equation

$$(\eta_0/\eta^{eff} - 1)(\underline{1} - \hat{k}\hat{k}) = \frac{9}{2}\,\phi\,(\underline{1} - \hat{k}\hat{k})\hat{k}:(\underline{T}_1 + \underline{T}_2 + \underline{T}_3):\hat{k}(\underline{1} - \hat{k}\hat{k}), \qquad (5.8)$$

with the definitions

$$\underline{T}_1 = -\frac{10}{9}\,\underline{\Delta}, \qquad (5.9)$$

$$\underline{T}_2 = \frac{100}{81}\, n_0 \lim_{\varepsilon\to 0} \int d\vec{r}\; g_0(r)\, e^{i\varepsilon\hat{k}\cdot\vec{r}}\, \underline{A}^{(2s,2s)}(\vec{r})\,, \qquad (5.10)$$

$$\underline{T}_3 = -\frac{125}{9}\, n_0 \int d\vec{r}\; g_0(r)(a/r)^6\, \underline{\Delta} : (2\hat{r}\hat{r}\hat{r}\hat{r} + \hat{r}\,\underline{1}\,\hat{r}) : \underline{\Delta}\,. \qquad (5.11)$$

Here $g_0(r)$ is the equilibrium pair distribution function to lowest order in the density,

$$g_0(r) = \begin{cases} 0 & \text{if } r \leqslant 2a \\ 1 & \text{if } r > 2a. \end{cases} \qquad (5.12)$$

The evaluation of $\underline{T}_2$ requires care because of the long range of the connector field $\underline{A}$. In terms of its Fourier transform we may write for this contribution

$$\underline{T}_2 = \frac{100}{81}\, n_0 \lim_{\varepsilon\to 0}\Big[\underline{A}^{(2s,2s)}(\varepsilon\hat{k}) + (2\pi)^{-3}\int d\vec{k}'\,\underline{A}^{(2s,2s)}(\vec{k}')\,\nu_0(|\varepsilon\hat{k}-\vec{k}'|)\Big], \qquad (5.13)$$

with

$$\nu_0(k) \equiv \int d\vec{r}\; e^{i\vec{k}\cdot\vec{r}}[g_0(r) - 1] = -16\pi a^2 k^{-1} j_1(2ak). \qquad (5.14)$$

Using expression (3.6) for the Fourier transformed connector field one finds, upon integration,

$$\underline{T}_2 = \frac{10}{9}\,\phi\left(5\underline{\Delta} : \hat{k}(\underline{1} - \hat{k}\hat{k})\hat{k} : \underline{\Delta} - \underline{\Delta}\right), \tag{5.15}$$

in the required limit $\varepsilon \to 0$. For the contribution $\underline{T}_3$ a straightforward integration of eq. (5.11) gives

$$\underline{T}_3 = -\frac{25}{24}\,\phi\,\underline{\Delta}\ . \tag{5.16}$$

Substituting the results (5.9), (5.15) and (5.16) into eq. (5.8), one finds for the effective viscosity at zero wavevector the equation

$$(\eta_o/\eta^{eff} - 1)(\underline{1} - \hat{k}\hat{k}) = [-\frac{5}{2}\,\phi + (\frac{5}{2}\,\phi)^2 - \frac{155}{32}\,\phi^2](\underline{1} - \hat{k}\hat{k}), \tag{5.17}$$

which gives the expansion to second order

$$\eta^{eff} = \eta_o[1 + \frac{5}{2}\,\phi + 4.84\,\phi^2 + \quad (\phi^3)], \tag{5.18}$$

found previously by Freed and Muthukumar[7] by a similar method (cf. section 1).

The importance of terms of order R^{-8} and higher in the hydrodynamic interactions between two spheres (not included in eq. (5.5)) has been investigated by Schmitz[6]. He obtained a value of 5.36 for the coefficient of the term of order ϕ^2, by including hydrodynamic interactions of order R^{-n} with $n \leqslant 15$. Although the coefficient in eq. (5.18) differs from this result by only 10%, the convergence appears to be rather slow: Schmitz estimates that terms of still higher order in 1/R can give further corrections of at most 5%. In the works of Peterson and Fixman[3] and Bedeaux, Kapral and Mazur[5] certain contributions from short-ranged hydrodynamic interactions are also included. These authors obtained values of 4.32 and 4.8 respectively.

The above results for the second order coefficient - which are all based on a multipole expansion of hydrodynamic interactions - may be compared with the value of 5.2 ± 0.3 obtained by Batchelor and Green[4], from an *exact* solution of the motion of two spheres in a linear flow field.

6. Expansion in correlation functions

In order to study the effective viscosity of a suspension which is not dilute, we shall adopt the method of expansion in correlation functions used in chs. II and III to calculate the diffusion coefficient of the suspended spheres. Formula (4.20) for $\eta(k)$ is the starting point of our analysis. Following ch. III, we now proceed to write this formula in terms of "renormalized" connectors, which account for the fact that (in an averaged sense) spheres interact hydrodynamically via the *suspension* - rather than through the pure fluid.

Let $\underline{\gamma}_0^{(n,n)}$ $(n = 1,2,3,\ldots)$ be an arbitrary constant tensor of rank $2n$. We denote by γ_0 the diagonal matrix with elements

$$\{\gamma_0\}_{n,m} = \delta_{nm}\, \underline{\gamma}_0^{(n,n)}. \qquad (6.1)$$

The matrix H_{γ_0} is defined - for each γ_0 - in terms of the matrix H (given in eq. (4.12)), by

$$H_{\gamma_0} \equiv H(1 - \gamma_0\, \underset{\sim}{Q}B^{-1} H)^{-1}. \qquad (6.2)$$

This matrix has elements

$$\{H_{\gamma_0}\}_{n,m} \equiv \begin{cases} \underline{T}_{\gamma_0}^{(n,m)} & \text{if } n=1 \text{ or } m=1 \\ \underline{A}_{\gamma_0}^{(n,m)} & \text{if } n\neq 1 \text{ and } m\neq 1, \end{cases} \qquad (6.3)$$

which are convolution operators with kernels $\underline{T}_{\gamma_0}^{(n,m)}(\vec{r})$ and $\underline{A}_{\gamma_0}^{(n,m)}(\vec{r})$ respectively. The latter kernel is identical to the *renormalized connector field* defined in ch. III.

We now choose $\underline{\gamma}_0^{(n,n)}$ to be a function of the average number density of the spheres n_0,

$$\underline{\gamma}_0^{(n,n)} - \underline{\gamma}_0^{(n,n)} \odot \underline{B}^{(n,n)^{-1}} \odot \underline{A}_{\gamma_0}^{(n,n)}(\vec{r}=0) = n_0\, \underline{1}^{(n,n)} \qquad (n\geq 2)^{*}. \qquad (6.4)$$

---

[*] The quantity $\underline{\gamma}_0^{(1,1)}$ does not play a role in the analysis and need not be further specified.

The tensor $\underline{1}^{(n,n)}$ used above is a generalized unit tensor of rank 2n,

$$\underline{1}^{(2,2)} = \underline{\Delta}, \quad \underline{1}^{(n,n)} = \underline{\Delta}^{(n-1,\mathrm{id},n-1)} \quad (n\geqslant 3), \tag{6.5}$$

where the $\underline{\Delta}$-tensors have been defined in eqs. (II-2.9) and (II-2.19). It has been shown in ch. III that $\underline{\gamma}_o^{(n,n)}$ is of the form

$$\underline{\gamma}_o^{(n,n)} = \gamma_o^{(n)}\, \underline{1}^{(n,n)}, \tag{6.6}$$

where $\gamma_o^{(n)}$ is a scalar function of n_o. The *renormalized "density"* $\gamma(\vec{r})$, with average γ_o, is given by

$$\gamma(\vec{r}) = \gamma_o n_o^{-1} n(\vec{r}); \tag{6.7}$$

the corresponding diagonal operator γ has kernel $\gamma(\vec{r})\delta(\vec{r}\,'-\vec{r})$.

We shall write formula (4.20) for the effective viscosity in terms of the renormalized connectors defined above, using the identity

$$\{\, H(\,1-n\,QB^{-1}\,H)^{-1}\}_{1,1} = \{\, H_{\gamma_o}(\,1-\delta\gamma\,QB^{-1}\,\overset{o}{H}_{\gamma_o})^{-1}\}_{1,1}. \tag{6.8}$$

The proof of this identity is very similar to that of eq. (III-3.7), given in the appendix of ch. III, and is therefore omitted here. The inverse operator on the r.h.s of the above equation contains fluctuations $\delta\gamma \equiv \gamma - \gamma_o$ and a matrix $\overset{o}{H}_{\gamma_o}$ with elements

$$\{\,\overset{o}{H}_{\gamma_o}\}_{n,m} = \begin{cases} \underline{\overset{o}{A}}_{\gamma_o}^{(n,n)} & \text{if } n=m\neq 1 \\[2ex] \{\, H_{\gamma_o}\}_{n,m} & \text{elsewise.} \end{cases} \tag{6.9}$$

Here the *cut-out* connector $\underline{\overset{o}{A}}_{\gamma_o}^{(n,n)}$ $(n\geqslant 2)$ has kernel

$$\underline{\overset{o}{A}}_{\gamma_o}^{(n,n)}(\vec{r}\,|\vec{r}\,') = \underline{\overset{o}{A}}_{\gamma_o}^{(n,n)}(\vec{r}\,'-\vec{r}) = \begin{cases} 0 & \text{if } \vec{r} = \vec{r}\,' \\[2ex] \underline{A}_{\gamma_o}^{(n,n)}(\vec{r}\,'-\vec{r}) & \text{if } \vec{r} \neq \vec{r}\,'. \end{cases} \tag{6.10}$$

Substitution of identity (6.8) into eq. (4.20) gives for $\eta(k)$ the alternative expression

$$\frac{1}{\eta(k)} \{ H \}_{1,1}(\vec{k}|\vec{k}') = \frac{1}{\eta_0} \langle \{ H_{\gamma_0} (1 - \delta\gamma\, \mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{H}_{\gamma_0})^{-1} \}_{1,1}(\vec{k}|\vec{k}') \rangle . \qquad (6.11)$$

Upon expansion of the inverse operator on the r.h.s. of eq. (6.11) in powers of $\delta\gamma$, one obtains an expansion for the reciprocal of the effective viscosity $\lambda(k) \equiv 1/\eta(k)$ in correlation functions of (renormalized) density fluctuations of increasing order

$$\lambda(k) = \lambda^{(0)}(k) + \lambda^{(2)}(k) + \ldots , \qquad (6.12)$$

where $\lambda^{(p)}(k)$ contains terms of order $\langle(\delta\gamma)^p\rangle$. Each term in this "fluctuation expansion" contains contributions from many-body hydrodynamic interactions of an arbitrary number of spheres. Furthermore, the renormalization of the density through eqs. (6.4) and (6.7) corresponds to an algebraic resummation of a class of self-correlations, cf. ch. III (section 3). As a result, the contributions from these special correlations are included in the zeroth order term.

We shall now give the expressions for the first two terms in the fluctuation expansion of $\lambda(k)$. To zeroth order one finds from eq. (6.11)

$$\lambda^{(0)}(k) \{ H \}_{1,1}(\vec{k}|\vec{k}') = \frac{1}{\eta_0} \{ H_{\gamma_0} \}_{1,1}(\vec{k}|\vec{k}'), \qquad (6.13)$$

or, by definition (4.12) and (6.3),

$$\lambda^{(0)}(k) \underline{T}^{(1,1)}(\vec{k}) = \frac{1}{\eta_0} \underline{T}_{\gamma_0}^{(1,1)}(\vec{k}). \qquad (6.13a)$$

The lowest order correction to the zeroth order result (6.13) is of order $\langle(\delta\gamma)^2\rangle$ (since terms linear in $\delta\gamma$ give a vanishing contribution after averaging) and is given by

$$\lambda^{(2)}(k) \{ H \}_{1,1}(\vec{k}|\vec{k}') = \frac{1}{\eta_0} \langle \{ H_{\gamma_0} \delta\gamma\, \mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{H}_{\gamma_0} \delta\gamma\, \mathcal{Q}\mathcal{B}^{-1} \overset{\circ}{H}_{\gamma_0} \}_{1,1}(\vec{k}|\vec{k}') \rangle . \qquad (6.14)$$

To evaluate the two-point correlation in this equation, we note that $\delta\gamma$ is given in terms of the density fluctuations $\delta n \equiv n - n_o$ by $\delta\gamma = \gamma_o n_o^{-1} \delta n$, cf. eq. (6.7). In view of the formula[16]

$$\langle \delta n(\vec{r}) \delta n(\vec{r}\,') \rangle = n_o \delta(\vec{r}\,' - \vec{r}) + n_o^2 [g(|\vec{r}\,' - \vec{r}|) - 1], \tag{6.15}$$

we find therefore*

$$\begin{aligned}\lambda^{(2)}(k)\underline{T}^{(1,1)}(\vec{k}) = {} & (\eta_o n_o)^{-1} \sum_{\substack{m,\ell=2\\ m\neq\ell}}^{\infty} \gamma_o^{(m)} \gamma_o^{(\ell)} \underline{T}_{\gamma_o}^{(1,m)}(\vec{k}) \odot \underline{B}^{(m,m)^{-1}} \odot \underline{A}_{\gamma_o}^{(m,\ell)}(\vec{r}=0) \\ & \odot \underline{B}^{(\ell,\ell)^{-1}} \odot \underline{T}^{(\ell,1)}(\vec{k}) + \frac{1}{\eta_o} \sum_{m,\ell=2}^{\infty} \gamma_o^{(m)} \gamma_o^{(\ell)} \underline{T}_{\gamma_o}^{(1,m)}(\vec{k}) \odot \underline{B}^{(m,m)^{-1}} \\ & \odot \Big(\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} \underline{A}_{\gamma_o}^{(m,\ell)}(\vec{r})[g(r)-1]\Big) \odot \underline{B}^{(\ell,\ell)^{-1}} \odot \underline{T}_{\gamma_o}^{(\ell,1)}(\vec{k}),\end{aligned} \tag{6.16}$$

where we have used that

$$\underline{\gamma}_o^{(m,m)} \odot \underline{B}^{(m,m)^{-1}} = \gamma_o^{(m)} \underline{B}^{(m,m)^{-1}}, \tag{6.17}$$

cf. eq. (6.6). The function $g(r)$ used in these equations is the equilibrium pair distribution function. Note that the above expression does not contain terms with factors $\underline{A}_{\gamma_o}^{(m,\ell)}(\vec{r}=0)$ with $\ell=m$, as a consequence of the cut (6.10). Indeed the contributions from these particular correlations (socalled diagonal ring self-correlations, cf. ch. III) are already accounted for in the zeroth order term $\lambda^{(0)}(k)$, through the renormalization of the density in eq. (6.4).

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*In the second term on the r.h.s. of this equation we have replaced in the integrand (for the case $\ell=m$) the cut-out connnector $\mathring{\underline{A}}_{\gamma_o}^{(m,\ell)}(\vec{r})$ by $\underline{A}_{\gamma_o}^{(m,\ell)}(\vec{r})$, since these two fields differ by a finite amount in a single point only, cf. definition (6.10).

7. Evaluation of the expansion in correlation functions to second order

To evaluate the first two terms of the expansion of $1/\eta(k)$ in correlation functions, we make use of representation (III-4.3) of the renormalized connector field $\underline{A}_{\gamma_o}^{(n,m)}(\vec{r})$ and of the corresponding expression for $\underline{T}_{\gamma_o}^{(n,m)}(\vec{r})$

$$\underline{T}_{\gamma_o}^{(n,m)}(\vec{r}) = (2\pi)^{-3} \int d\vec{k}\, e^{-i\vec{k}\cdot\vec{r}}\, \underline{T}^{(n,m)}(\vec{k})[1 + \phi S_{\gamma_o}(ak)]^{-1}, \tag{7.1}$$

where the function $S_{\gamma_o}(ak)$ has been defined in eq. (III-4.4). The renormalized density coefficients $\gamma_o^{(p)}$ ($p = 2,3,4,5$) have been determined as a function of n_o to a sufficient accuracy in ch. III, table 1. To calculate the effective viscosity we shall again use these values for $\gamma_o^{(p)}$; also, in the expressions for renormalized tensor fields we shall approximate $S_{\gamma_o}(ak)$ by $S_{\gamma_o}^{(5)}(ak)$, as defined in eq. (III-4.10). This latter function depends only on the values of $\gamma_o^{(p)}$ with $p \leqslant 5$. An estimate of the error introduced with this approximation is given below.

We are now in the position to evaluate the fluctuation expansion (6.12) of $\lambda(k) \equiv 1/\eta(k)$. To zeroth order one finds from eqs. (6.13) and (7.1)

$$\lambda^{(0)}(k) = \frac{1}{\eta_o} [1 + \phi S_{\gamma_o}(ak)]^{-1}. \tag{7.2}$$

In fig. 1 we have plotted, for five values of the volume fraction ϕ, the wavevector dependence of $\eta_o/\eta(k)$ to this order. The reciprocal of the effective viscosity increases monotonically as a function of the wavevector, from its small-k limit

$$\lim_{k\to 0} \lambda^{(0)}(k) = \frac{1}{\eta_o} \left(1 + \frac{5}{2}\, \phi\gamma_o^{(2)}/n_o\right)^{-1} \tag{7.3}$$

(cf. eq. (III-4.4)), to its large-k limit

$$\lim_{k\to\infty} \lambda^{(0)}(k) = 1/\eta_o, \tag{7.4}$$

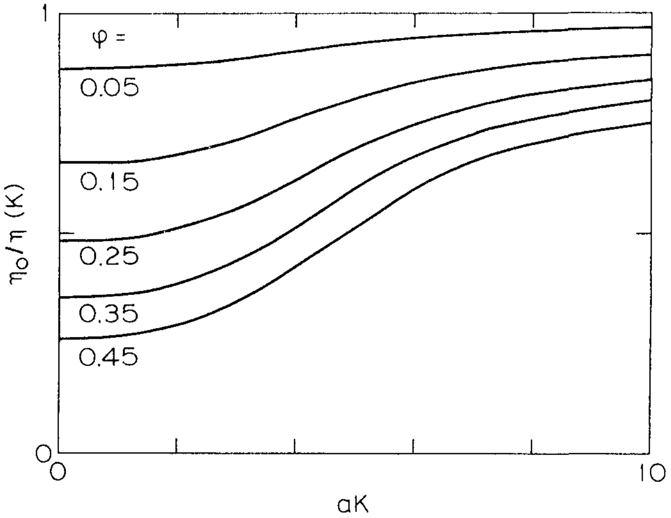

Fig. 1. Wavevector dependence of $\eta_o/\eta(k)$ for five values of the volume fraction ϕ, as results from eq. (7.2).

which is equal to the value at infinite dilution. (Note that the large-k limits of $\lambda^{(0)}(k)$ and $\lambda(k)$ are identical, cf. eq. (4.5).)

As mentioned above, the values plotted in fig. 1 are obtained by approximating the function $S_{\gamma_o}(ak)$ in eq. (7.2) by $S_{\gamma_o}^{(5)}(ak)$, defined in eq. (III-4.10). It has been checked that repeating the calculations to one lower order (approximating S_{γ_o} by $S_{\gamma_o}^{(4)}$ and using the values of $\gamma_o^{(p)}$ (p = 1,2,3,4) which correspond to this order of approximation, cf. section 4 in ch. III) would not change the results by more than 6%, over the whole range of wavevectors and densities. For not too large wavevectors (ak $\lesssim$ 3) the change is even less, viz. at most 2%.

We now return to the fluctuation expansion (6.12) of $\lambda(k)$, to evaluate the next (non-zero) term $\lambda^{(2)}(k)$, given by eq. (6.16). We shall only consider here the limiting behaviour of this term for small and large wavevectors.

Using the fact that $\underline{T}_{\gamma_o}^{(n,m)}(\vec{k})$ is of order k^{n+m-4} for small k (which follows from eqs. (3.4) and (7.1)) one finds that only one term on the r.h.s. of eq. (6.16) contributes to $\lambda^{(2)}(k)$ in the limit $k\to 0$, giving

$$\lim_{k\to 0} \lambda^{(2)}(k)(\underline{1} - \hat{k}\hat{k}) = \lim_{k\to 0} (6\pi\eta_o a)^{-1}\left(\gamma_o^{(2)}\right)^2 k^2\, \underline{T}_{\gamma_o}^{(1,2)}(\vec{k}) : \underline{B}^{(2,2)^{-1}}$$

$$: \left(\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \underline{A}_{\gamma_o}^{(2,2)}(\vec{r})[g(r)-1]\right) : \underline{B}^{(2,2)^{-1}} : \underline{T}_{\gamma_o}^{(2,1)}(\vec{k}), \qquad (7.5)$$

or explicitly

$$\lambda^{(2)}(k=0) = 20a^4\eta_o^{-1}\left(\gamma_o^{(2)}\right)^2 \left(1 + \tfrac{5}{2}\,\phi\gamma_o^{(2)}/n_o\right)^{-2} \int_0^\infty dq\; j_1^{\,2}(aq)$$

$$\times\ [1 + \phi S_{\gamma_o}(aq)]^{-1}\nu(q). \qquad (7.6)$$

In this last equation use has also been made of expression (III-4.3) for $\underline{A}_{\gamma_o}^{(2,2)}(\vec{r})$. We have furthermore defined

$$\nu(k) \equiv \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, [g(r) - 1]. \qquad (7.7)$$

Table 1

The fluctuation expansion (6.12) of $\lambda(k) \equiv 1/\eta(k)$ for $k=0$, as given by eqs. (7.3) and (7.6) to second order.

ϕ	$\eta_o\lambda^{(0)}(k=0)$	+ $\eta_o\lambda^{(2)}(k=0)$	= $\eta_o\lambda(k=0)$
0.05	0.879	- 0.005	0.87
0.10	0.765	- 0.017	0.75
0.15	0.661	- 0.030	0.63
0.20	0.568	- 0.042	0.53
0.25	0.486	- 0.051	0.44
0.30	0.416	- 0.057	0.36
0.35	0.355	- 0.060	0.30
0.40	0.304	- 0.060	0.24
0.45	0.261	- 0.058	0.20

To evaluate $\lambda^{(2)}(k=0)$ we have approximated the pair correlation function by the solution of the Percus-Yevick equation, found by Wertheim and Thiele[17] (an explicit analytic expression for $\nu(k)$ is given in ref. 18). The integral on the r.h.s. of eq. (7.12) was then computed numerically. Results are given in table 1.

To conclude this section we note that for large wavevectors the term $\lambda^{(2)}(k)$ goes to zero

$$\lim_{k\to\infty} \lambda^{(2)}(k) = 0, \tag{7.8}$$

as follows from eqs. (3.4),(6.16) and (7.1) (and might be expected on account of the fact, mentioned above, that $\lambda^{(0)}(k)$ and $\lambda(k)$ tend to the same limit as $k\to\infty$).

8. Discussion

We have calculated the wavevector dependent effective viscosity $\eta(k)$ of a suspension of spherical particles. This quantity relates the Fourier transforms of averaged velocity field and external field of force, cf. eq. (2.10). The validity of the present analysis is limited to a certain time scale or, alternatively, to a certain range of frequencies. More precisely, if we consider an external force which varies harmonically in time with frequency ω, the average response of the fluid is described by $\eta(k)$ in the regime

$$2\pi/\tau_C \ll \omega \ll a^{-2}\eta_0/\rho_0. \tag{8.1}$$

Here η_0 and ρ_0 are respectively the viscosity and mass density of the fluid, a is the radius of the suspended spheres and τ_C is the "configurational" relaxation time (see below).

The upper limit in eq. (8.1) is a consequence of our description of the motion of the fluid by the *quasi-static* Stokes equation (2.1), neglecting inertial effects (cf. ref. 2, § 24)*. For e.g. spheres of radius $a = 0.5\mu$ in water at room temperature, the upper limiting frequency $a^{-2}\eta_o/\rho_o$ is $4\cdot10^6$ Hz.

The lower limit to the frequency range in eq. (8.1) is due to the neglect of contributions from Brownian motion of the spheres: whereas in equilibrium this motion does not contribute - on the average - to the velocity field, a non-vanishing contribution remains if the distribution function of the configurations of the spheres is perturbed by an external force[19,20]. The validity of our analysis is therefore limited to a time scale much smaller than the time τ_C in which a configuration changes appreciably due to Brownian motion, since on this short time scale the deviation of the distribution function from its equilibrium form may be neglected (cf. a related discussion of time scales in theories of diffusion in ref. 21). The corresponding lower limiting frequency $2\pi/\tau_C$ is a few hundred Hertz at a volume fraction ϕ of the spheres of 0.45, for the system mentioned above. At lower concentrations, this frequency decreases and in fact to linear order in ϕ the viscosity is not affected by Brownian motion at all frequencies[19,20].

Having clarified the regime of validity of our analysis we now proceed to a discussion of our results. We have evaluated $\eta(k)$ through an expansion of its reciprocal in correlation functions of (renormalized) density fluctuations of increasing order (a socalled fluctuation expansion). The zeroth order result (7.2) in this expansion (shown in fig. 1) fully takes into account the many-body hydrodynamic interactions between an arbitrary number of spheres, as well as the resummed contributions from a class of self-correlations. For the case of zero wavevector we have evaluated moreover the next non-vanishing term in the fluctuation expansion (given by eq. (7.6)), which is of second order and is due to correlations between pairs of spheres. Results for

$$\eta^{eff} \equiv \lim_{k\to0} \eta(k) \tag{8.2}$$

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*For an analysis where inertial contributions to the effective viscosity are included, see ref. 5.

to this order are given in table 1.

It is interesting to compare these results for the concentration dependence of the effective viscosity at zero wavevector with the results from two simple formulae, which one can derive by making additional approximations.

The first formula

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi(1-\phi)^{-1} \tag{8.3}$$

can be obtained by completely neglecting correlations between the spheres, cf. appendix B. This formula gives values for η^{eff} which are considerably smaller - especially at large concentrations - than the results from the first two terms of the fluctuation expansion, cf. fig. 2 (where the reciprocal of η^{eff} is plotted). In these latter results, we recall, contributions from a class of self-correlations as well as from pair correlations are included. Formula (8.3) was first proposed by Saitô[22] (cf. also the derivations in refs. 5,6,9 and 23).

The second formula

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi(1 - \frac{5}{2}\,\phi)^{-1} \tag{8.4}$$

takes into account the same class of self-correlations which contributes to our zeroth order result (7.3) for η^{eff}. However, to arrive at eq. (8.4) these contributions are evaluated by an approximation of the hydrodynamic interactions between the spheres which in a way neglects their finite size, cf. appendix B. Whereas this socalled point-particle approximation correctly describes the interactions between the spheres if their separation is sufficiently large, it fails at smaller separations. Results obtained using this approximation will therefore become less and less reliable as the average separation of the spheres becomes smaller with increasing concentration. Indeed, as one can see from fig. 2, for large ϕ the values from eq. (8.4) deviate strongly from the results obtained using the full expressions for the hydrodynamic interactions. Note, in particular, that the effective viscosity according to eq. (8.4) has a pole at $\phi = 0.4$, whereas if one

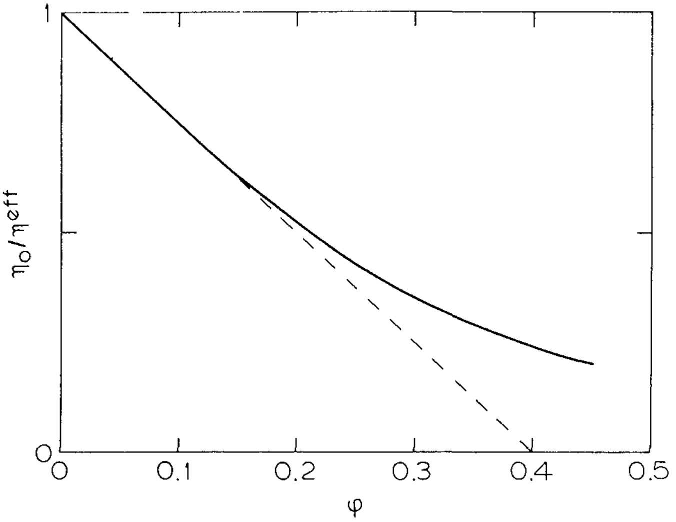

Fig. 2. Volume fraction dependence of the reciprocal of the effective viscosity at zero wavevector. The solid curve is taken from table 1, dotted and dashed curves from eqs. (8.3) and (8.4) respectively.

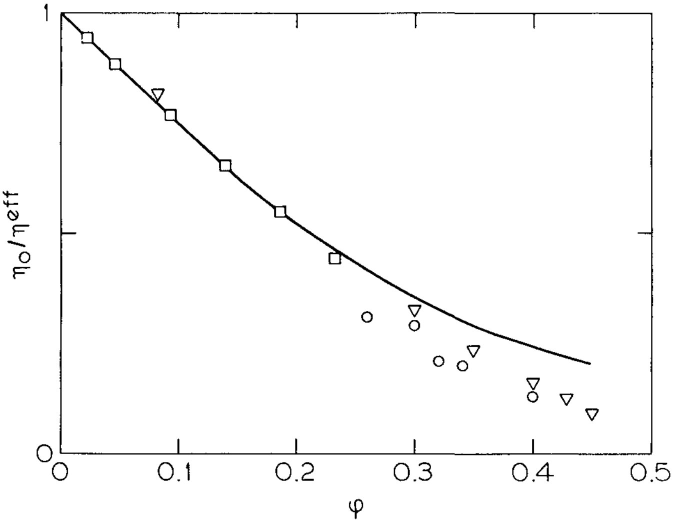

Fig. 3. ϕ-Dependence of η_o/η^{eff}. The solid curve is from table 1. Experimental data points are from refs. 28 (squares), 29 (triangles) and 30 (circles).

takes account of the finite size of the spheres the results remain bounded up to large volume fractions*.

Formula (8.4) was first derived by Lundgren[11] and more recently by several authors[8,9,10]. In the latter three derivations the suspension is treated as a mixture of two fluids, one fluid (with volume fraction ϕ) having an infinitely large viscosity, the other fluid having viscosity η_o. Clearly, in such a treatment no account is taken of the finite size of the suspended particles. The analysis of Lundgren, on the other hand - although leading to the same result (8.4) - proceeds from a different starting point and it is not clear to which extent the influence of the finite size of the spheres on their hydrodynamic interactions has been accounted for.

Before resuming the discussion of our results we mention still another formula for the concentration dependence of η^{eff}, derived by Mou and Adelman[27]. In this analysis some of the effects of the finite particle sizes are included, according to the authors. Numerically, their results are close to eq. (8.3) (and have for this reason not been plotted in fig. 2).

A comparison with experiments is possible for the small wavevector limit η^{eff} of the effective viscosity. In fig. 3 we show the data obtained by Saunders[28] and by Krieger and coworkers[29] for suspended spherical polystyrene latex particles. The radii of these particles where of the order of 0.1μ, with a narrow size distribution. Also shown are the data of Kops-Werkhoven and Fijnaut[30] for silica spheres of radius 0.07μ . If one compares these experimental results with the calculated values from table 1 (also plotted in fig. 3) one finds good agreement for volume fractions $\phi \lesssim 0.2$. At higher concentrations,

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*We mention in this connection that a pole in the plot of effective viscosity versus concentration has been found in two different contexts by Kapral and Bedeaux[24] (for a regular array of freely moving spheres) and by Muthukumar[25] (for randomly distributed immobile spheres). However, the validity of these results is questionable (for the same reason as in the present case of randomly distributed freely moving spheres), since in both these analyses higher order multipole contributions to the hydrodynamic interactions (resulting from the finite size of the spheres) were neglected (cf. also the discussion of the former analysis in ref. 26).

however, our calculations give values for η^{eff} which are considerably smaller than the experimental data. Two remarks are in order, which could each explain part of the discrepancy.

Firstly, we note that the expansion in correlation functions of the reciprocal of η^{eff} has only been evaluated to second order. In particular, contributions due to specific correlations between the positions of three or more spheres have not been included. The magnitude of these higher order terms can be estimated from the term of second order (due to two-sphere correlations), which is ~ 20% of the zeroth order result at the highest volume fractions considered (cf. table 1).

Secondly, we recall that - strictly speaking - our analysis is valid only on the short time scale $\tau \ll \tau_C$, in which Brownian motion has not yet affected a given configuration of the spheres. The measurements, on the other hand, were performed under static conditions. Theoretical studies of dilute suspensions have indeed shown* that the effect of Brownian motion is to increase η^{eff}. It would be interesting to perform dynamic measurements of the effective viscosity, in order to study, through its frequency dependence, the influence of Brownian motion.

9. The relation between effective viscosity and diffusion coefficient

In this section we shall compare the results for the wavevector *dependent effective viscosity* $\eta(k)$ *of a suspension obtained in this* ch., with those for the wavevector dependent (short-time) diffusion coefficient D(k) of the suspended spheres, obtained in ch. III. The latter quantity is given by eq. (III-2.1) and describes diffusion of the spheres on the time scale $\tau \ll \tau_C$ over which their positions are essentially constant (see e.g. ref. 21). The large wavevector limit of D(k) is the self-diffusion coefficient D_s, given by eq. (III-2.2).

In ch. III D(k) has been evaluated through an expansion in correlation functions of higher and higher order. As shown in section 7 of

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*The coefficient of the term of order ϕ^2 in the density expansion of η^{eff} increases due to Brownian motion by 20% to 6.2[19,20].

that chapter, the lowest order term in this expansion is given by eq. (III-2.1) - with the mobility tensor μ_{ij} which appears in this expression replaced by the *effective* pair mobility μ_{ij}^{eff} (cf. eq. (III-7.2))

$$\mu_{ij}^{eff} \equiv (2\pi)^{-3}\int d\vec{k}\; e^{-i\vec{k}\cdot\vec{R}_{ij}}\, \underline{A}^{(1,1)}(\vec{k})\, (6\pi a)^{-1}\lambda^{(0)}(k), \tag{9.1}$$

where the tensor $\underline{A}^{(1,1)}(\vec{k})$ has been defined in eq. (III-5.10); $\lambda^{(0)}(k)$ (defined in eq. (7.2)) is the zeroth order term in the expansion in correlation functions of the reciprocal of $\eta(k)$. Through the above equation effective viscosity and diffusion coefficient are related to each other.

This relation takes an especially simple form for the coefficient of self-diffusion D_s. To lowest order in the expansion in correlation functions, the mobility tensor in definition (III-2.2) of D_s may be replaced by expression (9.1) and one finds

$$D_s = k_BT\,\frac{1}{3}\,\pi^{-2}\int_0^\infty dk\left(\frac{\sin ak}{ak}\right)^2 \lambda^{(0)}(k). \tag{9.2}$$

Since the largest contribution to the integral in eq. (9.2) arises from the interval $0 \lesssim k \lesssim 1/a$ (and since $\lambda^{(0)}(k)$ is approximately constant in this interval, cf. fig. 1), one may approximate $\lambda^{(0)}(k)$ in the integrand by its small-k limit - which is the reciprocal of the effective viscosity at zero wavevector η^{eff} (to lowest order in the expansion in correlation functions). Upon integration one then finds

$$D_s \approx k_BT(6\pi\eta^{eff}a)^{-1}. \tag{9.3}$$

In fig. 4 we show the volume fraction dependence of D_s/D_o (where $D_o \equiv k_BT(6\pi\eta_o a)^{-1}$) and η_o/η^{eff}, resulting from an evaluation of the expansion in correlation functions for each of these quantities to second order. One sees that both quantities have a similar concentration dependence, in agreement with eq. (9.3). Deviations from this relation are due to: i) certain contributions from correlations; ii) wavevector dependence of the effective viscosity (a consequence of the

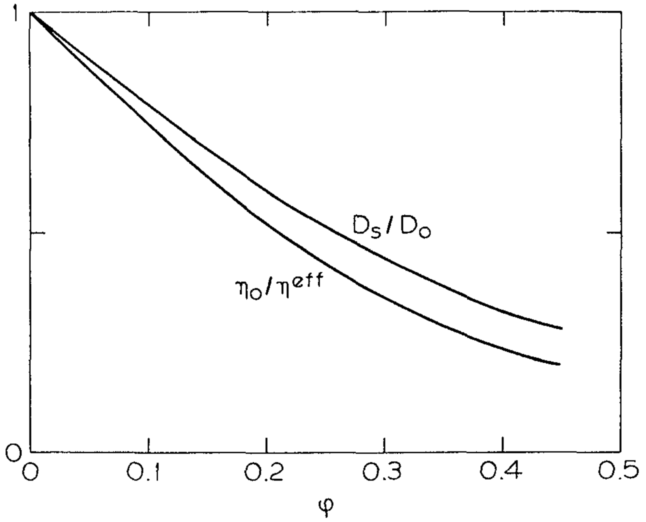

Fig. 4. Volume fraction dependence of the reciprocal of the effective viscosity at zero wavevector η^{eff} (from table 1) and of the self-diffusion coefficient (from table 3 of ch. III).

finite size of the particles).

We have discussed here the relation between effective viscosity and diffusion coefficient on the short time scale $\tau \ll \tau_C$. Experimentally, this relation has been investigated only on the long time scale $\tau \gg \tau_C$ [30,31]: it has been observed that the product of self-diffusion coefficient and effective viscosity is approximately independent of the concentration, confirming - on this time scale - a relation of the form (9.3).

Appendix A. Elimination of the induced forces

According to eqs. (7.2) and (7.3) of the paper by Mazur and van Saarloos[12], one has for the irreducible multipole moments of the induced forces on the spheres the following hierarchy of equations* $(i = 1,2,\ldots N)$

$$\underline{F}_i^{(p)} = 6\pi\eta_0 a(2p-1)!!\,\underline{B}^{(p,p)^{-1}} \odot \overline{\ulcorner \hat{n}_i^{p-1} \urcorner\, \vec{v}_0}^{S_i} + \sum_{m=2}^{\infty} \sum_{\substack{j=1\\ j\neq i}}^{N} \underline{B}^{(p,p)^{-1}} \odot \underline{A}_{ij}^{(p,m)} \odot \underline{F}_j^{(m)} \qquad (p\geq 2). \qquad (A.1)$$

(Here with $\underline{F}^{(2)}$ only the symmetric and traceless part of this second moment is implied.) The surface moment of the unperturbed velocity field $\vec{v}_0$ on the r.h.s. of this equation is defined as follows

$$\overline{\ulcorner \hat{n}_i^{m} \urcorner\, \vec{v}_0}^{S_i} \equiv (4\pi a^2)^{-1} a^{-m} \int d\vec{r}\, \ulcorner(\vec{r} - \vec{R}_i)^m\urcorner\, \vec{v}_0(\vec{r})\delta(|\vec{r}-\vec{R}_i| - a). \qquad (A.2)$$

In the present case, the unperturbed flow is given in terms of the external force by

$$\vec{v}_0(\vec{k}) \equiv (\eta_0 k^2)^{-1}(\underline{1} - \hat{k}\hat{k})\cdot\vec{F}^{ext}(\vec{k}). \qquad (A.3)$$

The formal solution of the hierarchy (A.1) is of the form

$$\underline{F}_i^{(p)} = 6\pi\eta_0 a \sum_{m=2}^{\infty} \sum_{j=1}^{N} (2m-1)!!\,\underline{\zeta}_{ij}^{(p,m)} \odot \overline{\ulcorner \hat{n}_j^{m-1} \urcorner\, \vec{v}_0}^{S_j} \qquad (p\geq 2), \qquad (A.4)$$

with the generalized friction tensor $\underline{\zeta}_{ij}^{(p,m)}$ given by eq. (3.2).

The transverse part of the induced force is given in terms of the moments considered above by the expansion (cf. ref. 12, eq. (3.14))

$$(\underline{1} - \hat{k}\hat{k})\cdot\vec{F}_i^{ind}(\vec{k}) = \sum_{p=2}^{\infty} (2p-1)!!\, i^{1-p} j_{p-1}(ak)(\underline{1} - \hat{k}\hat{k})\, \ulcorner \hat{k}^{p-1} \urcorner \odot \underline{F}_i^{(p)}. \qquad (A.5)$$

For the surface moments of the unperturbed flow, furthermore, we have

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*The tensor $\underline{B}^{(2,2)^{-1}}$ used here corresponds to $\underline{B}^{(2s,2s)^{-1}}$ in ref. 12. Note furthermore that (in view of eq. (2.4)) both the first moments and the anti-symmetric parts of the second moments of the induced forces are zero and consequently do not appear in eq. (A.1).

the identity (ref. 12, eq. (4.1))*

$$\overline{\hat{n}_i^{\lceil p \rceil}\, \vec{v}_o}^{S_i} = (2\pi)^{-3} i^p \int d\vec{k}\; e^{i\vec{k}\cdot\vec{R}_i}\, j_p(ak)\, \hat{k}^{\lceil p \rceil}\, \vec{v}_o(\vec{k}). \tag{A.6}$$

Eqs. (A.3)-(A.6) yield for the velocity field given by eq. (2.7) the result

$$6\pi\eta_o a\, \vec{v}(\vec{k}) = \underline{T}^{(1,1)}(\vec{k})\cdot\vec{F}^{ext}(\vec{k}) + \sum_{i,j=1}^{N} \sum_{n,m=2}^{\infty} e^{-i\vec{k}\cdot\vec{R}_i}\, \underline{T}^{(1,n)}(\vec{k})$$

$$\odot\, \underline{\zeta}_{ij}^{(n,m)} \odot (2\pi)^{-3} \int d\vec{k}'\, e^{i\vec{k}'\cdot\vec{R}_j}\, \underline{T}^{(m,1)}(\vec{k}')\cdot\vec{F}^{ext}(\vec{k}'), \tag{A.7}$$

with the tensor field $\underline{T}$ defined in eq. (3.4). This equation implies for the kernel $\underline{M}$, defined in eq. (2.8), the expression (3.1).

Appendix B. Derivation of formulae (8.3) and (8.4) for η^{eff}

1. Formula (8.3) (no correlations)

In order to arrive at formula (8.3) for the zero wavevector effective viscosity η^{eff}, we first redefine the connector field $\underline{A}^{(2,2)}(\vec{r})$ in the following way

$$\underline{A}_o^{(2,2)}(\vec{r}) \equiv \underline{A}^{(2,2)}(\vec{r})\, g_o(r), \tag{B.1}$$

where the function $g_o(r)$ was defined in eq. (5.12). Note that, since $\underline{A}_o(\vec{r})$ and $\underline{A}(\vec{r})$ are identical for $r>2a$, we may replace the latter field by the former in definition (II-2.4) of the connector $\underline{A}_{ij}$.

Next consider eq. (4.7) for η^{eff}. If we completely neglect correlations, this expression (together with eqs. (3.2) and (II-2.6)) gives†

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*Note that, with respect to the formulae in ref. 12, we have made the substitution (II-2.11).

†The tensor $\underline{\Delta}$ used in this eq. is identical to the tensor $\underline{\Delta}^{(2,2)}$ defined in eq. (II-2.10).

$$(\eta_o/\eta^{eff} - 1)(\underline{1}-\hat{k}\hat{k}) = -5\phi(\underline{1}-\hat{k}\hat{k})\hat{k}:\Big[\underline{\Delta} + \lim_{\varepsilon\to 0}\sum_{p=1}^{\infty}\Big(-\frac{10}{9}\,n_o\,\underline{A}_o^{(2s,2s)}(\varepsilon\hat{k})\Big)^p\Big]$$

$$:\hat{k}(\underline{1} - \hat{k}\hat{k}). \qquad \text{(B.2)}$$

Here we have used the fact that $\underline{A}^{(n,m)}(\varepsilon\hat{k})$ is of order ε^{n+m-4} (cf. eq. (II-2.15)), so that eq. (B.2) does not contain contributions from connectors with upper indices $n+m>4$. From eqs. (5.10) and (5.15) we see that

$$-\frac{10}{9}\,n_o \lim_{\varepsilon\to 0}\underline{A}_o^{(2s,2s)}(\varepsilon\hat{k}) = \phi\big(\underline{\Delta} - 5\underline{\Delta}:\hat{k}(\underline{1} - \hat{k}\hat{k})\hat{k}:\underline{\Delta}\big), \qquad \text{(B.3)}$$

and hence

$$(\eta_o/\eta^{eff} - 1)(\underline{1} - \hat{k}\hat{k}) = -5\phi(\underline{1} - \hat{k}\hat{k})\hat{k}:\big[(1-\phi)\underline{\Delta} + 5\phi\underline{\Delta}:\hat{k}(\underline{1} - \hat{k}\hat{k})\hat{k}:\underline{\Delta}\big]^{-1}$$

$$:\hat{k}(\underline{1} - \hat{k}\hat{k}) = -\frac{5}{2}\,\phi\Big(1 + \frac{3}{2}\,\phi\Big)^{-1}(\underline{1} - \hat{k}\hat{k}). \qquad \text{(B.4)}$$

Eq. (B.4) implies that

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi(1-\phi)^{-1}, \qquad \text{(B.5)}$$

which is Saitô's formula (8.3).

We remark that if one would replace the function $g_o(r)$ in eq. (B.1) by some other function of $\vec{r}$ which is unity for $r>2a$, one would obtain an alternative formula for the effective viscosity in the absence of correlations. To decide which expression for the connector field for $r \leqslant 2a$ gives the most accurate results in this approximation, one would have to compare the magnitude of the corrections from correlations. We can, however, make the following observation: the particular choice made above accounts to some extent for the impenetrability of the spheres, since the connector field $\underline{A}_o^{(2,2)}(\vec{r})$ vanishes for $r<2a$. One might expect, therefore, the resulting formula (B.5) to be more accurate than – for instance – a formula which one would obtain by replacing $g_o(r)$ in eq. (B.1) by unity *for all* r. Indeed, in this latter case one finds upon neglecting correlations the result

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi, \tag{B.6}$$

which is inferior to eq. (B.5).

2. Formula (8.4) (point-particle approximation)

Consider the zeroth order result (7.3) for the effective viscosity at k=0,

$$\eta^{eff}/\eta_o = 1 + \frac{5}{2}\,\phi\gamma_o^{(2)}/n_o, \tag{B.7}$$

where $\gamma_o^{(2)}$ is given as a function of n_o through eq. (III-4.9)

$$\gamma_o^{(2)} - \gamma_o^{(2)}\ \phi\,\frac{6}{\pi}\int_0^\infty dk\ j_1^2(k)\ S_{\gamma_o}(k)[1 + \phi S_{\gamma_o}(k)]^{-1} = n_o. \tag{B.8}$$

The function $S_{\gamma_o}(k)$ behaves for small k as (cf. eq. (III-4.4))

$$S_{\gamma_o}(k) = \frac{5}{2}\,\gamma_o^{(2)}/n_o + \mathcal{O}(k^2). \tag{B.9}$$

If in the integral in eq. (B.8) one would approximate this function by its zero-k limit, one would find for $\gamma_o^{(2)}$

$$\gamma_o^{(2)} = n_o(1 - \frac{5}{2}\,\phi)^{-1}, \tag{B.10}$$

which gives (with eq. (B.7)) formula (8.4) for the effective viscosity.

Since the wavevector dependence of the function $S_{\gamma_o}(k)$ which renormalizes the connectors (according to eq. (III-4.3)) is a consequence of the finite radius of the spheres, the above approximation - which neglects this k-dependence - may be called in this sense a point-particle approximation.

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SAMENVATTING

De doelstelling van het onderzoek beschreven in dit proefschrift, is de bestudering van de invloed van *hydrodynamische interacties* op transporteigenschappen van suspensies. Hiertoe wordt de concentratie-afhankelijkheid van diffusiecoëfficiënt en effectieve viscositeit van gesuspendeerde "harde bollen" onderzocht (op een korte tijdschaal waarop de posities van de bollen niet noemenswaardig veranderen).

Het grote struikelblok bij de behandeling van hydrodynamische interacties is de essentiële niet-additiviteit van deze koppelingen via de vloeistof. Dat een beperking tot additieve paar-interacties in niet-verdunde suspensies ongerechtvaardigd is, werd in dit onderzoek voor de eerste maal expliciet aangetoond, door berekening van de zelf-diffusie coëfficiënt tot op tweede orde in de concentratie (zie hoofdstuk II). (Van experimentele zijde zijn P. Pusey en W. van Megen door metingen van deze grootheid tot dezelfde conclusie gekomen.) Een theorie die geldig is ook buiten het verdunde regime, zal daarom rekening moeten houden met niet-additieve hydrodynamische interacties tussen een willekeurig aantal deeltjes. Met het oog hierop werd een techniek van hersommatie van veel-deeltjes hydrodynamische interacties ontwikkeld, gebruik makend van een door P. Mazur en W. van Saarloos gegeven methode om hydrodynamische stroming langs meerdere bollen te analyseren. Op betrouwbare wijze konden dan transporteigenschappen van geconcentreerde suspensies berekend worden via een zogenoemde *fluctuatie-ontwikkeling*. Dit is een ontwikkeling in correlatiefuncties van dichtheidsfluctuaties van hogere en hogere orde.

In hoofdstuk II wordt deze fluctuatie-ontwikkeling uiteengezet in haar meest eenvoudige vorm, voor het geval van zelf-diffusie. De laagste orde term in deze ontwikkeling bevat de gehersommeerde bijdragen van hydrodynamische interacties tussen 2,3,4,5,... bollen - in de afwezigheid van enige correlaties. Hogere orde termen bevatten correcties op dit resultaat ten gevolge van correlaties tussen fluctuaties in de concentratie der bollen. Deze correcties zijn belangrijk, in het bijzonder bij de hoogst beschouwde concentraties.

Om deze reden wordt in hoofdstuk III een tweede fluctuatieontwikkeling ondezocht, die men uit de eerste kan verkrijgen door een gedeeltelijke hersommering van hogere orde correlaties. De laagste orde term van deze alternatieve ontwikkeling bevat reeds de bijdragen van een belangrijke klasse van zelf-correlaties (dat zijn die correlaties, die aanwezig zouden zijn in het hypothetische geval van doordringbare bollen). Zowel een vergelijking met experimenten als ook een berekening van de eerstvolgende term in de ontwikkeling geven aan, dat deze laagste orde term betrouwbare resultaten geeft voor de diffusiecoëfficiënt over een breed concentratiebereik. Het derde hoofdstuk wordt besloten met een interpretatie van de laagste orde resultaten in termen van een *effectieve* paar-interactie.

In hoofdstuk IV wordt de effectieve viscositeit van de suspensie bestudeerd, volgens dezelfde methode die in het vorige hoofdstuk was toegepast op diffusie. In het verleden is bij de studie van de viscositeit van suspensies herhaaldelijk gebruik gemaakt van een benadering die de eindige afmetingen van de gesuspendeerde deeltjes verwaarloost. Hoewel deze benadering te verdedigen is voor voldoende verdunde systemen, leidt zij tot volkomen foutieve resultaten bij hogere concentraties - zoals expliciet aangetoond in hoofdstuk IV. Tot besluit worden in dit hoofdstuk de behaalde resultaten voor diffusie en viscositeit vergeleken. In het bijzonder wordt onderzocht een (voor de eerste maal door D.J. Cebula en medewerkers waargenomen) empirische relatie tussen zelf-diffusie coëfficiënt en effectieve viscositeit, welke inhoudt dat het produkt van deze beide grootheden bij benadering onafhankelijk is van de concentratie.

CURRICULUM VITAE

van Carlo Willem Joannes Beenakker,
geboren op 9 juni 1960 te Leiden

Na mijn eindexamen gymnasium β aan het Stedelijk Gymnasium te Leiden begon ik in 1978 mijn studie aan de Rijksuniversiteit te Leiden. In januari 1981 legde ik het kandidaatsexamen Natuurkunde en Wiskunde met bijvak Scheikunde af. Het doctoraal examen Natuurkunde met bijvak Wiskunde en onderwijsbevoegdheden in de wis- en natuurkunde volgde met lof in juni 1982. Voor dit examen verrichtte ik experimenteel werk in de werkgroep voor de studie van Moleculen in Aangeslagen Toestand, onder leiding van Prof.dr. J. Schmidt. Bij mijn theoretisch doctoraal onderzoek op het Instituut-Lorentz voor Theoretische Natuurkunde werd, onder leiding van Prof.dr. P. Mazur, een aanvang gemaakt met het onderzoek van de theorie van transporteigenschappen van suspensies. Dit onderzoek werd voortgezet in september 1982, als wetenschappelijk medewerker in dienst van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.). De behaalde resultaten zijn beschreven in dit proefschrift.

Aan het onderwijs droeg ik bij door in het academisch jaar 1983/1984 Prof.dr. D. Bedeaux te assisteren bij de organisatie van een studentenseminarium over hydrodynamica. Tevens hielp ik bij het afnemen van tentamens en gaf ik enkele werkcolleges.

Financiële steun van de Stichting F.O.M. stelde mij in staat deel te nemen aan een bijeenkomst over suspensies van de Britse "Royal Society of Chemistry" (Loughborough, 1983) en aan de zomerschool over "Fundamental Problems in Statistical Mechanics VI" (Trondheim, 1984). Voor de handelingen van deze school maakte ik een dictaat van de colleges van Prof.dr. J.S. Langer over de kinetiek van fasenovergangen.

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   To be published.

Apart from minor modifications, chapters II, III and IV of this thesis are contained in the publications 2, 4 and 6 respectively.