

**THE EFFECTIVE VISCOSITY OF A CONCENTRATED
SUSPENSION OF SPHERES
(AND ITS RELATION TO DIFFUSION)**

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A theory is given for the concentration and wave vector dependence of the effective viscosity of a suspension of spherical particles. The analysis is valid up to high concentrations and fully takes into account the many-body hydrodynamic interactions between an arbitrary number of spheres. The relation to the diffusion coefficient of the spheres is discussed.

1. Introduction

The concentration dependence of the effective viscosity η^{eff} of a suspension of spherical particles in a fluid (with viscosity η_0) 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

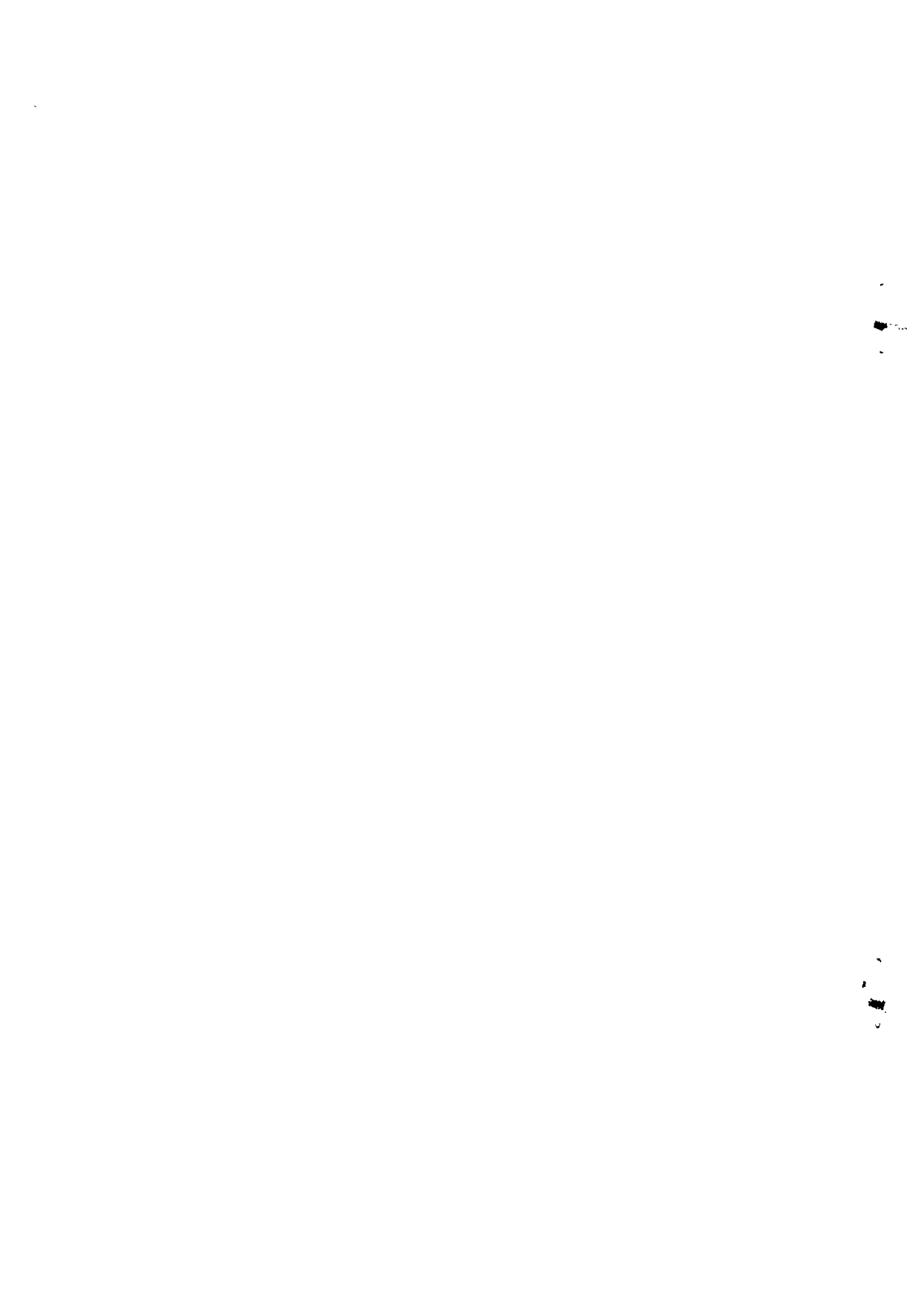
$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi + 5.2\phi^2. \quad (1.1)$$

The coefficient of the linear term was first calculated by Einstein¹⁾ (cf. also ref. 2); the quadratic term has been evaluated by several authors³⁻⁷⁾, the value given in eq. (1.1) being due to Batchelor and Green⁴⁾ (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 (both theoretically⁸⁾ and experimentally⁹⁾) 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 equations of motion in the presence of more than two spheres, an approximation which

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



neglects the finite size of the spheres is customary. Several authors¹¹⁻¹³), 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_0 . This approach yields a very simple formula for the effective viscosity*

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi(1 - \frac{5}{2}\phi)^{-1}, \quad (1.2)$$

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 paper.

In this paper 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 Saarloos¹⁵), 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 was used by Mazur and the author in the context of diffusion^{16,17}).

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 so-called method of induced forces^{18,19})) differs from the conventional approach where the perturbations of an externally imposed *flow* are considered. To obtain the effective viscosity by this second method (used e.g. by Peterson and Fixman³), one must find both the average stress and 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 Muthukumar⁷), 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 Saarloos¹⁵) (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

* This same formula was first derived by Lundgren¹⁴), from a different starting point.

concentration is from this point on straightforward. (The zero-wave-vector results given in this section were previously obtained by Freed and Muthukumar⁷⁾ 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 ref. 17. 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 wave vector and concentration dependence of $\eta(k)$ are given in fig. 1 and table I. 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 coefficient¹⁷⁾ 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_0 . We describe the motion of the fluid by the quasi-static Stokes equation, which – within the context of the method of induced forces^{18,19)} – reads

$$\nabla p(\mathbf{r}) - \eta_0 \Delta \mathbf{v}(\mathbf{r}) = \mathbf{F}^{\text{ext}}(\mathbf{r}) + \sum_{j=1}^N \mathbf{F}_j^{\text{ind}}(\mathbf{r}), \quad (2.1)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}) = 0. \quad (2.1a)$$

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

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

$$\mathbf{v}(\mathbf{r}) = \mathbf{u}_j + \boldsymbol{\omega}_j \wedge (\mathbf{r} - \mathbf{R}_j) \quad \text{for } |\mathbf{r} - \mathbf{R}_j| \leq a, \quad (2.3)$$

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

so that the velocity of the fluid satisfies stick boundary conditions on the surfaces of the spheres. In these equations \mathbf{R}_j is the position-vector of the center of sphere j , and \mathbf{u}_j and $\boldsymbol{\omega}_j$ 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

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

(where we have furthermore assumed that $\mathbf{F}^{\text{ext}}(\mathbf{r})$ 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 $\mathbf{v}(\mathbf{r})$,

$$\mathbf{v}(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{v}(\mathbf{r}), \quad (2.5)$$

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

$$\mathbf{F}_j^{\text{ind}}(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_j)} \mathbf{F}_j^{\text{ind}}(\mathbf{r}). \quad (2.6)$$

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

$$\mathbf{v}(\mathbf{k}) = (\eta_0 k^2)^{-1} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \left[\mathbf{F}^{\text{ext}}(\mathbf{k}) + \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{R}_j} \mathbf{F}_j^{\text{ind}}(\mathbf{k}) \right]. \quad (2.7)$$

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

Following the general scheme of Mazur and van Saarloos¹⁵), 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

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{M}(\mathbf{r} | \mathbf{r}') \cdot \mathbf{F}^{\text{ext}}(\mathbf{r}'). \quad (2.8)$$

An explicit expression for the tensor $\mathbf{M}(\mathbf{r} | \mathbf{r}')$ 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 $\langle \mathbf{M}(\mathbf{r} | \mathbf{r}') \rangle$ will depend on the separation $\mathbf{r}' - \mathbf{r}$ 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

$$\langle \mathbf{M}(\mathbf{r} | \mathbf{r}') \rangle = (2\pi)^{-3} \int d\mathbf{k} e^{-i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})} (\eta(k) k^2)^{-1} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}), \quad (2.9)$$

giving for the macroscopic velocity the expression

$$\langle \mathbf{v}(\mathbf{k}) \rangle = (\eta(k) k^2)^{-1} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \mathbf{F}^{\text{ext}}(\mathbf{k}). \quad (2.10)$$

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 $\mathbf{F}^{\text{ext}}(\mathbf{k})$ in an incompressible fluid with viscosity $\eta(k)$.

3. Results from the hydrodynamic analysis

As we show in appendix A, the tensor $\mathbf{M}(\mathbf{r} | \mathbf{r}')$ —which relates the velocity at point \mathbf{r} to the external force density at point \mathbf{r}' (eq. (2.8))—may straightforwardly be derived from the results of Mazur and van Saarloos¹⁵. One finds the expression

$$\begin{aligned} 6\pi\eta_0 a \mathbf{M}(\mathbf{r} | \mathbf{r}') &= \mathbf{T}^{(1,1)}(\mathbf{r}' - \mathbf{r}) + \sum_{n,m=2}^{\infty} \sum_{i,j=1}^N \mathbf{T}^{(1,n)}(\mathbf{R}_i - \mathbf{r}) \odot \zeta_y^{(n,m)} \\ &\odot \mathbf{T}^{(m,1)}(\mathbf{r}' - \mathbf{R}_j), \end{aligned} \quad (3.1)$$

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

$$\begin{aligned} \zeta_y^{(n,m)} &= \mathbf{B}^{(n,n)^{-1}} \delta_{nm} \delta_y + \mathbf{B}^{(n,n)^{-1}} \odot \mathbf{A}_y^{(n,m)} \odot \mathbf{B}^{(m,m)^{-1}} (1 - \delta_y) \\ &+ \sum_{s=1}^{\infty} \sum_{p_1=2}^{\infty} \sum_{p_2=2}^{\infty} \cdots \sum_{\substack{p_s=2 \\ j_1 \neq 1 \\ j_2 \neq j_1}}^{\infty} \sum_{j_1=1}^N \sum_{j_2=1}^N \cdots \sum_{\substack{j_s=1 \\ j_s \neq j_{s-1}}}^N \mathbf{B}^{(n,p_1)^{-1}} \odot \mathbf{A}_{j_1}^{(n,p_1)} \\ &\odot \mathbf{B}^{(p_1,p_1)^{-1}} \odot \mathbf{A}_{j_1 j_2}^{(p_1,p_2)} \odot \cdots \odot \mathbf{B}^{(p_s,p_s)^{-1}} \odot \mathbf{A}_{j_s}^{(p_s,m)} \odot \mathbf{B}^{(m,m)^{-1}}. \end{aligned} \quad (3.2)$$

The objects $\zeta_{ij}^{(n,m)}$, $\mathbf{T}^{(n,m)}(\mathbf{r})$, $\mathbf{A}_y^{(n,m)}$ and $\mathbf{B}^{(n,m)^{-1}}$ in the above equations are tensors of rank $n + m$. The dot \odot in e.g. $\mathbf{A}_y^{(n,m)} \odot \mathbf{B}^{(m,m)^{-1}}$ 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 \mathbf{T} , \mathbf{A} and \mathbf{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 well-known Oseen tensor (see below). The perturbation of the fluid flow by the spheres is accounted for by the generalized (dimensionless) friction tensors $\zeta_{ij}^{(n,m)}$, 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, $\zeta_{ii}^{(n,m)}$ 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 \mathbf{A} and \mathbf{B}^{-1} in eq. (3.2). This series constitutes an expansion in inverse powers of the interparticle separation, in view of the following property¹⁵⁾ of the ‘‘connectors’’ $\mathbf{A}_{ij}^{(n,m)}$ (defined for $i \neq j$)

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

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

We shall now give the definitions of the tensors occurring in eqs. (3.1) and (3.2). The general expression for the connectors

$$\mathbf{A}_{ij}^{(n,m)} = \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{R}_i - \mathbf{r}) \delta(\mathbf{R}_j - \mathbf{r}') \mathbf{A}^{(n,m)}(\mathbf{r}' - \mathbf{r}) \quad (i \neq j, R_{ij} > 2a) \tag{3.4}$$

is in terms of the connector field $\mathbf{A}^{(n,m)}(\mathbf{r})$, given by

$$\mathbf{A}^{(n,m)}(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{A}^{(n,m)}(\mathbf{k}), \tag{3.5}$$

with

$$\mathbf{A}^{(n,m)}(\mathbf{k}) = 6\pi a i^{n-m} (2n-1)!! (2m-1)!! k^{-2} j_{n-1}(ak) j_{m-1}(ak) \widehat{\mathbf{k}}^{n-1} (\mathbf{1} - \widehat{\mathbf{k}}\widehat{\mathbf{k}}) \widehat{\mathbf{k}}^{m-1}, \tag{3.6}$$

cf. refs. 15 and 16. We have used here the notation $(2n-1)!! \equiv 1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-3) \cdot (2n-1)$; j_p denotes a spherical Bessel function* ; $\widehat{\mathbf{k}}^p$

* This function is related to the Bessel function of order $p + \frac{1}{2}$ by $j_p(x) = (\frac{1}{2}\pi/x)^{1/2} J_{p+1/2}(x)$.

represents 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 $\hat{\mathbf{k}}$ (For useful formulae concerning irreducible tensors, see ref. 20) For $p = 1, 2$ one has e.g.

$$\overline{\hat{\mathbf{k}}} = \hat{\mathbf{k}}, \quad \overline{\hat{\mathbf{k}}\hat{\mathbf{k}}} = \hat{\mathbf{k}}\hat{\mathbf{k}} - \frac{1}{3}\mathbf{1} \quad (3.7)$$

The ‘‘propagator’’ $\mathbf{T}^{(n,m)}(\mathbf{r})$ is defined in terms of its Fourier transform (cf. eq. (3.5)) by

$$\mathbf{T}^{(n,m)}(\mathbf{k}) = 6\pi a_1^{n-m} (2n-1)!! (2m-1)!! k^{2j'_{n-1}(ak)} j'_{m-1}(ak) \overline{\hat{\mathbf{k}}^{n-1}} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \overline{\hat{\mathbf{k}}^{m-1}}, \quad (3.8)$$

with the definition

$$j'_p(x) = J_p(x) \quad \text{for } p \geq 1, \quad j'_0(x) \equiv 1 \quad (3.9)$$

Finally we give expressions for the constant tensor $\mathbf{B}^{(n,n)}$ ($n \geq 2$), cf. refs. 15 and 16,

$$\mathbf{B}^{(2,2)} = -\frac{10}{9}\mathbf{\Delta}, \quad (3.10)$$

$$\begin{aligned} \mathbf{B}^{(n,n)} = & -\frac{2}{3} [(n-1)!(2n-3)!!]^{-1} \left(\mathbf{\Delta}^{(n-1 \text{ id } n-1)} + \frac{n}{n+1} \mathbf{\Delta}^{(n,n)} \right. \\ & \left. + \left(\frac{n-1}{n-2} \right) \left(\frac{2n-3}{2n-1} \right) \mathbf{\Delta}^{(n-1 \text{ } n-1)} \circ^{n-2} \mathbf{\Delta}^{(n-1 \text{ } n-1)} \right) \quad (n \geq 3), \end{aligned} \quad (3.10a)$$

where the symbol \circ^p denotes a p -fold contraction. The class of tensors $\mathbf{\Delta}^{(n,n)}$ of rank $2n$ used in these equations (with the abbreviation $\mathbf{\Delta}^{(2,2)} \equiv \mathbf{\Delta}$) project out the irreducible part of a tensor of rank n

$$\mathbf{\Delta}^{(n,n)} \circ \mathbf{b}^n = \mathbf{b}^n \circ \mathbf{\Delta}^{(n,n)} = \overline{\mathbf{b}^n} \quad (3.11)$$

For $n = 1, 2$ one has e.g. 20)

$$\mathbf{\Delta}^{(1,1)} = \delta_{\mu\nu}, \quad \mathbf{\Delta}^{(2,2)} \equiv \mathbf{\Delta}_{\mu\nu\kappa\lambda} = \frac{1}{2}\delta_{\mu\lambda}\delta_{\nu\kappa} + \frac{1}{2}\delta_{\mu\kappa}\delta_{\nu\lambda} - \frac{1}{3}\delta_{\mu\nu}\delta_{\kappa\lambda} \quad (3.12)$$

In eq. (3.10a) we have also used the tensor $\mathbf{\Delta}^{(n-1 \text{ id } n-1)}$ of rank $2n$ with elements

$$\mathbf{\Delta}^{(n-1 \text{ id } n-1)}_{\mu_1 \mu_{n-1} \kappa\lambda \nu_1 \nu_{n-1}} = \delta_{\kappa\lambda} \mathbf{\Delta}^{(n-1 \text{ } n-1)}_{\mu_1 \mu_{n-1} \nu_1 \nu_{n-1}} \quad (3.13)$$

This tensor acts as a unit tensor when contracted with the first n indices of the tensors $\mathbf{A}^{(n,m)}$ or $\mathbf{T}^{(n,m)}$, e.g.

$$\Delta^{(n-1,\text{id},n-1)} \odot^n \mathbf{A}_y^{(n,m)} = \mathbf{A}_y^{(n,m)}. \quad (3.14)$$

To conclude this section we give two formulae (derived in ref. 16) for the tensors defined above:

$$\mathbf{A}^{(n,p)}(\mathbf{k}) \odot \mathbf{B}^{(p,p)^{-1}} \odot \mathbf{A}^{(p,m)}(\mathbf{k}) = -6\pi a^3 \mathbf{A}^{(n,m)}(\mathbf{k}) \varepsilon_p (2p-1)^2 (ak)^{-2} j_{p-1}^2(ak) \quad (p \geq 2), \quad (3.15)$$

$$\sum_{p=2}^{\infty} \mathbf{A}^{(n,p)}(\mathbf{k}) \odot \mathbf{B}^{(p,p)^{-1}} \odot \mathbf{A}^{(p,m)}(\mathbf{k}) = -\frac{4}{3} \pi a^3 S(ak) \mathbf{A}^{(n,m)}(\mathbf{k}), \quad (3.16)$$

with the definitions

$$\varepsilon_2 = 5/9, \quad \varepsilon_p = 1 \quad (p \geq 3), \quad (3.17)$$

$$S(x) \equiv \sum_{p=2}^{\infty} \frac{9}{2} \varepsilon_p (2p-1)^2 x^{-2} j_{p-1}^2(x) = \frac{9}{2} [x^{-1} \text{Si}(2x) + \frac{1}{2} x^{-2} \cos(2x) + \frac{1}{4} x^{-3} \sin(2x) - x^{-4} \sin^2 x - 4x^{-6} (\sin x - x \cos x)^2]. \quad (3.18)$$

The sine-integral $\text{Si}(x)$ is defined by

$$\text{Si}(x) = \int_0^x t^{-1} \sin t \, dt. \quad (3.19)$$

We remark that formulae (3.15) and (3.16) remain valid if one replaces each tensor \mathbf{A} in these equations by the tensor \mathbf{T} .

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

$$\mathbf{M}(\mathbf{k} | \mathbf{k}') = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \int d\mathbf{r}' e^{i\mathbf{k}'\cdot\mathbf{r}'} \mathbf{M}(\mathbf{r} | \mathbf{r}') \quad (4.1)$$

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

$$6\pi\eta_0 a \mathbf{M}(\mathbf{k} | \mathbf{k}') = (2\pi)^3 \delta(\mathbf{k}' - \mathbf{k}) \mathbf{T}^{(1)}(\mathbf{k}) + \sum_{n=m-2}^{\infty} \sum_{l,j=1}^N \mathbf{T}^{(l,n)}(\mathbf{k}) \circ e^{i\mathbf{k} \cdot \mathbf{R}_l} \zeta_y^{(n,m)} e^{i\mathbf{k}' \cdot \mathbf{R}_j} \circ \mathbf{T}^{(m,1)}(\mathbf{k}') \quad (4.2)$$

From translational invariance of ζ_y and of the distribution function it follows that (for an infinite system¹)

$$\left\langle \sum_{l,j=1}^N e^{-i\mathbf{k} \cdot \mathbf{R}_l} \zeta_y^{(n,m)} e^{i\mathbf{k}' \cdot \mathbf{R}_j} \right\rangle = n_0 (2\pi)^3 \delta(\mathbf{k}' - \mathbf{k}) \left\langle N^{-1} \sum_{l,j=1}^N \zeta_y^{(n,m)} e^{i\mathbf{k} \cdot \mathbf{R}_j} \right\rangle, \quad (4.3)$$

where $n_0 = N/V$ 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

$$6\pi a (\eta_0/\eta(k) - 1) (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = n_0 k^2 \sum_{n=m-2}^{\infty} \mathbf{T}^{(1,n)}(\mathbf{k}) \circ \left\langle N^{-1} \sum_{l,j=1}^N \zeta_y^{(n,m)} e^{i\mathbf{k} \cdot \mathbf{R}_j} \right\rangle \circ \mathbf{T}^{(m,1)}(\mathbf{k}) \quad (4.4)$$

Use has also been made here of the explicit expression for $\mathbf{T}^{(1,1)}(\mathbf{k})$ (eq (3.8)). One may verify (using the fact that $\mathbf{k} \cdot \mathbf{T}^{(1,n)}(\mathbf{k}) = 0$ for all n , cf eq (3.8)) that the r.h.s. of eq (4.4) is the product of a scalar function of k and the tensor $\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}$, 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_0 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 $k \rightarrow \infty$ (cf eq (3.8)), so that in this limit the effective viscosity is equal to its value at infinite dilution

$$\lim_{k \rightarrow \infty} \eta(k) = \eta_0 \quad (4.5)$$

This limiting behaviour reflects the fact that for large wave vectors the Fourier transformed velocity field remains almost unperturbed by the presence of the spheres

* That is to say in the limit $N, V \rightarrow \infty, N/V = n_0 = \text{constant}$

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

$$\eta^{\text{eff}} \equiv \lim_{k \rightarrow 0} \eta(k) \quad (4.6)$$

From the fact that $\mathbf{T}^{(rs)}(\mathbf{k})$ is of order k^{r+s-4} for small k (cf. eq. (3.8)) it follows that only the term with $n = m = 2$ in the series on the r.h.s. of eq. (4.4) gives a nonvanishing contribution in the limit $k \rightarrow 0$. For η^{eff} we therefore have the more simple formula

$$(\eta_0/\eta^{\text{eff}} - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = \lim_{\epsilon \rightarrow 0} \frac{9}{2} \phi (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \hat{\mathbf{k}} \left\langle N^{-1} \sum_{j=1}^N \zeta_{ij}^{(2,2)} e^{i\epsilon \mathbf{k} \cdot \mathbf{R}_{ij}} \right\rangle \hat{\mathbf{k}} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}), \quad (4.7)$$

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

$$\phi = \frac{4}{3} \pi a^3 n_0 \quad (4.8)$$

Eqs. (4.4) and (4.7) are a most convenient starting point for the calculation of the (wave vector 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 a similar context^{16,17)}

First we redefine the connector field in the following way

$$\tilde{\mathbf{A}}^{(nm)}(\mathbf{r}) = \mathbf{A}^{(nm)}(\mathbf{r}) \quad \text{if } \mathbf{r} \neq 0, \quad \tilde{\mathbf{A}}^{(nm)}(\mathbf{r} = 0) \equiv 0 \quad (4.9)$$

Next we introduce convolution operators $\tilde{\mathbf{A}}^{(nm)}$ and $\mathbf{T}^{(nm)}$ with kernels

$$\tilde{\mathbf{A}}^{(nm)}(\mathbf{r} | \mathbf{r}') = \tilde{\mathbf{A}}^{(nm)}(\mathbf{r}' - \mathbf{r}), \quad (4.10)$$

$$\mathbf{T}^{(nm)}(\mathbf{r} | \mathbf{r}') = \mathbf{T}^{(nm)}(\mathbf{r} - \mathbf{r}'), \quad (4.11)$$

and a matrix \mathcal{H} of which these operators are the elements

$$\{\mathcal{H}\}_{nm} = \begin{cases} \mathbf{T}^{(nm)} & \text{if } n = 1 \text{ or } m = 1, \\ \tilde{\mathbf{A}}^{(nm)} & \text{if } n \neq 1 \text{ and } m \neq 1 \end{cases} \quad (4.12)$$

We further define a matrix \mathcal{B}^{-1} with elements

$$\{\mathcal{B}^{-1}\}_{n,m} = \delta_{nm} \mathbf{B}^{(n,n)^{-1}} \quad (4.13)$$

and a projection matrix Q by

$$\{Q\}_{n,m} = \delta_{nm} - \delta_{n1} \delta_{m1}. \quad (4.14)$$

Finally, the microscopic density field

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{R}_i) \quad (4.15)$$

corresponds to the diagonal operator n ,

$$n(\mathbf{r} | \mathbf{r}') = n(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r}). \quad (4.16)$$

With these notations we may write e.g.

$$\begin{aligned} & \sum_{m=2}^{\infty} \sum_{i=1}^N \mathbf{T}^{(1,m)}(\mathbf{R}_i - \mathbf{r}) \odot \mathbf{B}^{(m,m)^{-1}} \odot \mathbf{T}^{(m,1)}(\mathbf{r}' - \mathbf{R}_i) \\ &= \sum_{m=2}^{\infty} \int d\mathbf{r}_1 \mathbf{T}^{(1,m)}(\mathbf{r}_1 - \mathbf{r}) n(\mathbf{r}_1) \odot \mathbf{B}^{(m,m)^{-1}} \odot \mathbf{T}^{(m,1)}(\mathbf{r}' - \mathbf{r}_1) \\ &= \{\mathcal{H} n Q \mathcal{B}^{-1} \mathcal{H}\}_{1,1}(\mathbf{r} | \mathbf{r}'). \end{aligned} \quad (4.17)$$

Similarly one has

$$\begin{aligned} & \sum_{m,k=2}^{\infty} \sum_{\substack{i,j=1 \\ i \neq j}}^N \mathbf{T}^{(1,m)}(\mathbf{R}_i - \mathbf{r}) \odot \mathbf{B}^{(m,m)^{-1}} \odot \mathbf{A}_{ij}^{(m,k)} \odot \mathbf{B}^{(k,k)^{-1}} \odot \mathbf{T}^{(k,1)}(\mathbf{r}' - \mathbf{R}_j) \\ &= \{\mathcal{H} n Q \mathcal{B}^{-1} \mathcal{H} n Q \mathcal{B}^{-1} \mathcal{H}\}_{1,1}(\mathbf{r} | \mathbf{r}'). \end{aligned} \quad (4.18)$$

In these equations the kernel is taken of the 1,1 element of the matrix of operators between braces. For the kernel $\mathbf{M}(\mathbf{r} | \mathbf{r}')$ we now have in this compact notation

$$6\pi\eta_0 a \mathbf{M}(\mathbf{r} | \mathbf{r}') = \{\mathcal{H}(1 - n Q \mathcal{B}^{-1} \mathcal{H})^{-1}\}_{1,1}(\mathbf{r} | \mathbf{r}'). \quad (4.19)$$

Indeed, by expanding the operator between braces in this equation in powers

of n , we have eqs (4 17) and (4 18) as the first and second order terms From the complete series we recover the expression for $\mathbf{M}(\mathbf{r} | \mathbf{r}')$ given in eqs (3 1) and (3 2)

From eqs (2 9) and (4 19) we thus find for the effective viscosity $\eta(k)$ the operator formula

$$\frac{1}{\eta(k)} \{\mathcal{H}\}_{11}(\mathbf{k} | \mathbf{k}') = \frac{1}{\eta_0} \langle \{\mathcal{H}(1 - nQ\mathcal{B}^{-1}\mathcal{H})^{-1}\}_{11}(\mathbf{k} | \mathbf{k}') \rangle, \quad (4 20)$$

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 we find from eqs (3 2) and (4 4)

$$6\pi a(\eta_0/\eta(k) - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = n_0 k^2 \sum_{m=2}^{\infty} \mathbf{T}^{(1\ m)}(\mathbf{k}) \circ \mathbf{B}^{(m\ m)^{-1}} \circ \mathbf{T}^{(m\ 1)}(\mathbf{k}) \quad (5 1)$$

The series in this equation may be summed analytically, cf formula (3 16) and the subsequent remark The result is

$$(\eta_0/\eta(k) - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = -\phi S(ak)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}), \quad (5 2)$$

where the function $S(x)$ has been defined in eq (3 18) Eq (5 2) implies

$$\eta(k) = \eta_0 [1 + \phi S(ak) + \mathcal{O}(\phi^2)], \quad (5 3)$$

representing an extension of Einstein's¹²⁾ formula for the effective viscosity at zero wavevector to arbitrary values of k For small k , the function $S(ak)$ behaves as

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

as follows from expansion of the r.h.s. of eq. (3.18). 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 et al.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^{6,21)}, 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 wave vector 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 $\zeta_y^{(2,2)}$ we find, restricting ourselves to these terms (cf. also eqs. (3.3) and (3.10)),

$$\begin{aligned} \zeta_y^{(2,2)} = & -\frac{10}{9} \delta_y \mathbf{\Delta} + \left(-\frac{10}{9}\right)^2 (1 - \delta_y) \mathbf{A}_y^{(2s,2s)} \\ & + \left(-\frac{10}{9}\right)^3 \delta_y \sum_{k \neq i} R_{ik}^{-6} \mathbf{G}_{ik}^{(2s,2s)} : \mathbf{G}_{ki}^{(2s,2s)} + \mathcal{O}(R^{-8}), \end{aligned} \quad (5.5)$$

to eighth order in the expansion in inverse powers of the separation of the spheres R^* . The connector $\mathbf{A}^{(2s,2s)} \equiv \mathbf{\Delta} : \mathbf{A}^{(2,2)} : \mathbf{\Delta}$ 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 $\mathbf{G}_{ik}^{(2s,2s)}$ is given by¹⁵⁾

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

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

$$\left(-\frac{10}{9}\right)^3 R_{ik}^{-6} \mathbf{G}_{ik}^{(2s,2s)} : \mathbf{G}_{ki}^{(2s,2s)} = -\frac{125}{9} (a/R_{ik})^6 \mathbf{\Delta} : (2 \hat{\mathbf{r}}_{ik} \hat{\mathbf{r}}_{ik} \hat{\mathbf{r}}_{ik} \hat{\mathbf{r}}_{ik} + \hat{\mathbf{r}}_{ik} \mathbf{1} \hat{\mathbf{r}}_{ik}) : \mathbf{\Delta}. \quad (5.7)$$

The above equations enable us to calculate the zero wave vector 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

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

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

with the definitions

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

$$\mathbf{T}_2 = \frac{100}{81}n_0 \lim_{\varepsilon \rightarrow 0} \int d\mathbf{r} g_0(r) e^{i\varepsilon\hat{\mathbf{k}}\cdot\mathbf{r}} \mathbf{A}^{(2s,2s)}(\mathbf{r}), \quad (5.10)$$

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

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

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

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

$$\mathbf{T}_2 = \frac{100}{81}n_0 \lim_{\varepsilon \rightarrow 0} \left[\mathbf{A}^{(2s,2s)}(\varepsilon\hat{\mathbf{k}}) + (2\pi)^{-3} \int d\mathbf{k}' \mathbf{A}^{(2s,2s)}(\mathbf{k}) \nu_0(|\varepsilon\hat{\mathbf{k}} - \mathbf{k}'|) \right], \quad (5.13)$$

with

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

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

$$\mathbf{T}_2 = \frac{10}{9}\phi(5\Delta : \hat{\mathbf{k}}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\hat{\mathbf{k}} : \Delta - \Delta), \quad (5.15)$$

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

$$\mathbf{T}_3 = -\frac{25}{24}\phi\Delta. \quad (5.16)$$

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

$$(\eta_0/\eta^{\text{eff}} - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = \left[-\frac{5}{2}\phi + \left(\frac{5}{2}\phi\right)^2 - \frac{155}{32}\phi^2 \right](\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}), \quad (5.17)$$

which gives the expansion to second order

$$\eta^{\text{eff}} = \eta_0 \left[1 + \frac{5}{2}\phi + 4.84\phi^2 + \mathcal{O}(\phi^3) \right], \quad (5.18)$$

found previously by Freed and Muthukumar⁷⁾ 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 Schmitz⁶⁾. 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 $n \leq 15$. 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 Fixman³⁾ and Bedeaux et al.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 Green⁴⁾, 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 refs. 16 and 17 to calculate the diffusion coefficient of the suspended spheres. Formula (4.20) for $\eta(k)$ is the starting point of our analysis. Following ref. 17, 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 $\gamma_0^{(n,n)}$ ($n = 1, 2, 3, \dots$) be an arbitrary constant tensor of rank $2n$. We denote by γ_0 the diagonal matrix with elements

$$\{\gamma_0\}_{n,m} = \delta_{nm} \gamma_0^{(n,n)}. \quad (6.1)$$

The matrix \mathcal{H}_{γ_0} is defined – for each γ_0 – in terms of the matrix \mathcal{H} (given in eq. (4.12)) by

$$\mathcal{H}_{\gamma_0} \equiv \mathcal{H}(1 - \gamma_0 Q \mathcal{B}^{-1} \mathcal{H})^{-1}. \quad (6.2)$$

This matrix has elements

$$\{\mathcal{H}_{\gamma_0}\}_{n,m} \equiv \begin{cases} \mathbf{T}_{\gamma_0}^{(n,m)} & \text{if } n = 1 \text{ or } m = 1, \\ \mathbf{A}_{\gamma_0}^{(n,m)} & \text{if } n \neq 1 \text{ and } m \neq 1, \end{cases} \quad (6.3)$$

which are convolution operators with kernels $\mathbf{T}_{\gamma_0}^{(n,m)}(\mathbf{r})$ and $\mathbf{A}_{\gamma_0}^{(n,m)}(\mathbf{r})$ respectively. The latter kernel is identical to the *renormalized connector* defined in ref. 17.

We now choose $\gamma_0^{(n,n)}$ to be a function of the average number density of the spheres n_0 ,

$$\gamma_0^{(n,n)} - \gamma_0^{(n,n)} \odot \mathbf{B}^{(n,n)^{-1}} \odot \mathbf{A}_{\gamma_0}^{(n,n)}(\mathbf{r} = 0) = n_0 \mathbf{1}^{(n,n)} \quad (n \geq 2)^* \quad (6.4)$$

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

$$\mathbf{1}^{(2,2)} = \mathbf{\Delta}, \quad \mathbf{1}^{(n,n)} = \mathbf{\Delta}^{(n-1, \text{id}, n-1)} \quad (n \geq 3), \quad (6.5)$$

where the $\mathbf{\Delta}$ -tensors have been defined in eqs. (3.11)–(3.13). It has been shown in ref. 17 that $\gamma_0^{(n,n)}$ is of the form

$$\gamma_0^{(n,n)} = \gamma_0^{(n)} \mathbf{1}^{(n,n)}, \quad (6.6)$$

where $\gamma_0^{(n)}$ is a scalar function of n_0 . The *renormalized “density”* $\gamma(\mathbf{r})$, with average γ_0 , is given by

$$\gamma(\mathbf{r}) = \gamma_0 n_0^{-1} n(\mathbf{r}); \quad (6.7)$$

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

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

$$\{\mathcal{H}(1 - n Q \mathcal{B}^{-1} \mathcal{H})^{-1}\}_{1,1} = \{\mathcal{H}_{\gamma_0}(1 - \delta \gamma Q \mathcal{B}^{-1} \mathcal{H}_{\gamma_0}^{\circ})^{-1}\}_{1,1}, \quad (6.8)$$

* The quantity $\gamma_0^{(1,1)}$ does not play a role in the analysis and need not be further specified.

cf. appendix B. The inverse operator on the r.h.s of the above equation contains fluctuations $\delta\gamma \equiv \gamma - \gamma_0$ and a matrix $\overset{\circ}{\mathcal{H}}_{\gamma_0}$ with elements

$$\{\overset{\circ}{\mathcal{H}}_{\gamma_0}\}_{n,m} = \begin{cases} \overset{\circ}{\mathbf{A}}_{\gamma_0}^{(n,n)} & \text{if } n = m \neq 1, \\ \{\mathcal{H}_{\gamma_0}\}_{n,m} & \text{elsewise.} \end{cases} \quad (6.9)$$

Here the *cut-out* connector $\overset{\circ}{\mathbf{A}}_{\gamma_0}^{(n,n)}$ ($n \geq 2$) has kernel

$$\overset{\circ}{\mathbf{A}}_{\gamma_0}^{(n,n)}(\mathbf{r} | \mathbf{r}') = \overset{\circ}{\mathbf{A}}_{\gamma_0}^{(n,n)}(\mathbf{r}' - \mathbf{r}) = \begin{cases} 0 & \text{if } \mathbf{r} = \mathbf{r}', \\ \mathbf{A}_{\gamma_0}^{(n,n)}(\mathbf{r}' - \mathbf{r}) & \text{if } \mathbf{r} \neq \mathbf{r}'. \end{cases} \quad (6.10)$$

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

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

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

$$\lambda(k) = \lambda^{(0)}(k) + \lambda^{(2)}(k) + \dots, \quad (6.12)$$

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. ref. 17 (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)

$$\lambda^{(0)}(k) \{\mathcal{H}\}_{1,1}(\mathbf{k} | \mathbf{k}') = \frac{1}{\eta_0} \{\mathcal{H}_{\gamma_0}\}_{1,1}(\mathbf{k} | \mathbf{k}'), \quad (6.13)$$

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

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

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

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

To evaluate the two-point correlation in this equation, we note that $\delta\gamma$ is given in terms of the density fluctuations $\delta n \equiv n - n_0$ by $\delta\gamma = \gamma_0 n_0^{-1} \delta n$, cf. eq. (6.7). In view of the formula²²⁾

$$\langle \delta n(\mathbf{r}) \delta n(\mathbf{r}') \rangle = n_0 \delta(\mathbf{r}' - \mathbf{r}) + n_0^2 [g(|\mathbf{r}' - \mathbf{r}|) - 1], \quad (6.15)$$

we find therefore^{*}

$$\begin{aligned} \lambda^{(2)}(\mathbf{k}) \mathbf{T}^{(1,1)}(\mathbf{k}) &= (\eta_0 \eta_0)^{-1} \sum_{\substack{m,l=2 \\ m \neq l}}^{\infty} \gamma_0^{(m)} \gamma_0^{(l)} \mathbf{T}_{\gamma_0}^{(l,m)}(\mathbf{k}) \odot \mathbf{B}^{(m,m)^{-1}} \\ &\odot \mathbf{A}_{\gamma_0}^{(m,l)}(\mathbf{r}=0) \odot \mathbf{B}^{(l,l)^{-1}} \odot \mathbf{T}^{(l,1)}(\mathbf{k}) \\ &+ \frac{1}{\eta_0} \sum_{m,l=2}^{\infty} \gamma_0^{(m)} \gamma_0^{(l)} \mathbf{T}_{\gamma_0}^{(1,m)}(\mathbf{k}) \odot \mathbf{B}^{(m,m)^{-1}} \odot \left(\int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{A}_{\gamma_0}^{(m,l)}(\mathbf{r}) \right. \\ &\left. \times [g(\mathbf{r}) - 1] \right) \odot \mathbf{B}^{(l,l)^{-1}} \odot \mathbf{T}_{\gamma_0}^{(l,1)}(\mathbf{k}), \end{aligned} \quad (6.16)$$

where we have used that

$$\gamma_0^{(m,m)} \odot \mathbf{B}^{(m,m)^{-1}} = \gamma_0^{(m)} \mathbf{B}^{(m,m)^{-1}}, \quad (6.17)$$

cf. eq. (6.6). The function $g(\mathbf{r})$ used in these equations is the equilibrium pair distribution function. Note that the above expression does not contain terms with factors $\mathbf{A}_{\gamma_0}^{(m,l)}(\mathbf{r}=0)$ with $l = m$, as a consequence of the cut (6.10). Indeed the contributions from these particular correlations (so-called diagonal ring-self-correlations, cf. ref. 17) are already accounted for in the zeroth order term $\lambda^{(0)}(\mathbf{k})$, through the renormalization of the density in eq. (6.4).

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

In order to evaluate the first two terms of the expansion of $1/\eta(\mathbf{k})$ in

^{*} In the second term on the r.h.s. of this equation we have replaced in the integrand (for the case $l = m$) the cut-out connector $\hat{\mathbf{A}}_{\gamma_0}^{(m,l)}(\mathbf{r})$ by $\mathbf{A}_{\gamma_0}^{(m,l)}(\mathbf{r})$, since these two fields differ by a finite amount in a single point only, cf. definition (6.10).

correlation functions, we make use of the following representation of the renormalized tensor fields (defined in eqs (6 2) and (6 3))

$$\mathbf{T}_{\gamma_0}^{(nm)}(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{T}^{(nm)}(\mathbf{k}) [1 + \phi S_{\gamma_0}(ak)]^{-1}, \quad (7 1)$$

$$\mathbf{A}_{\gamma_0}^{(nm)}(\mathbf{r}) = \tilde{\mathbf{A}}^{(nm)}(\mathbf{r}) - (2\pi)^{-3} \int d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{A}^{(nm)}(\mathbf{k}) \phi S_{\gamma_0}(ak) [1 + \phi S_{\gamma_0}(ak)]^{-1}, \quad (7 2)$$

with the definition

$$S_{\gamma_0}(ak) = \sum_{p=2}^{\infty} \frac{1}{2} \varepsilon_p \gamma_0^{(p)} n_0^{-1} (2p-1)^2 (ak)^{-2} J_{p-1}^2(ak) \quad (7 3)$$

The symbol ε_p used in this last equation has been defined in eq (3 17) The above expressions follow from an evaluation of the inverse operator in eq (6 2), utilizing eqs (3 15) (see also the subsequent remark) and (6 17), cf refs 16 and 17 We shall use in particular the value of the renormalized connector field $\mathbf{A}_{\gamma_0}^{(nn)}(\mathbf{r})$ at $\mathbf{r} = 0$, given by

$$\mathbf{B}^{(nn)} \circ \mathbf{A}_{\gamma_0}^{(nn)}(\mathbf{r} = 0) = \frac{2}{\pi} (2n-1) \mathbf{1}^{(nn)} \int_0^{\infty} dk J_{n-1}^2(k) \phi S_{\gamma_0}(k) [1 + \phi S_{\gamma_0}(k)]^{-1}, \quad (7 4)$$

where the tensor $\mathbf{1}^{(nn)}$ has been defined in eq (6 5) The above formula is obtained by performing the angular integration in eq (7 2), cf refs 16 and 17

The coefficients $\gamma_0^{(p)}$ in the series in eq (7 3) are given as a function of the density n_0 by the equations

$$\gamma_0^{(p)} - \gamma_0^{(p)} \phi (2p-1) \frac{2}{\pi} \int_0^{\infty} dk J_{p-1}^2(k) S_{\gamma_0}(k) [1 + \phi S_{\gamma_0}(k)]^{-1} = n_0 \quad (p = 2, 3, \dots), \quad (7 5)$$

according to eqs (6 4), (6 17) and (7 4) This infinite set of coupled equations has been solved to a sufficient accuracy in ref 17, by approximating $S_{\gamma_0}(k)$ by

$$S_{\gamma_0}^{(L)}(k) \equiv S(k) + \sum_{p=2}^L \frac{1}{2} \varepsilon_p (\gamma_0^{(p)} - n_0) n_0^{-1} (2p-1)^2 k^{-2} J_{p-1}^2(k), \quad (7 6)$$

for a given number $L = 2, 3, 4, \dots$. The function $S(k)$ appearing in this definition is given explicitly in eq. (3.18). From this equation and definition (7.3) of $S_{\gamma_0}(k)$ it follows that

$$\lim_{L \rightarrow \infty} S_{\gamma_0}^{(L)}(k) = S_{\gamma_0}(k). \tag{7.7}$$

With the above approximation the $L - 1$ equations for $\gamma_0^{(p)}$ ($p = 2, 3, \dots, L$) in (7.5) decouple and may be solved numerically. In table I of ref. 17, the values of $\gamma_0^{(p)}$ ($p = 2, 3, 4, 5$) are given which have been obtained by this procedure with $L = 5$.

To calculate the effective viscosity $\eta(k)$ we shall use these values for $\gamma_0^{(p)}$; also, in expressions (7.1) and (7.2) for the renormalized tensor fields we shall approximate $S_{\gamma_0}(ak)$ by $S_{\gamma_0}^{(5)}(ak)$, as defined in eq. (7.6). 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, cf. ref. 17 (section 4). We shall return to this point 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)

$$\lambda^{(0)}(k) = \frac{1}{\eta_0} [1 + \phi S_{\gamma_0}(ak)]^{-1}. \tag{7.8}$$

In fig. 1 we have plotted, for five values of the volume fraction ϕ , the wave vector dependence of $\eta_0/\eta(k)$ to this order. The reciprocal of the effective

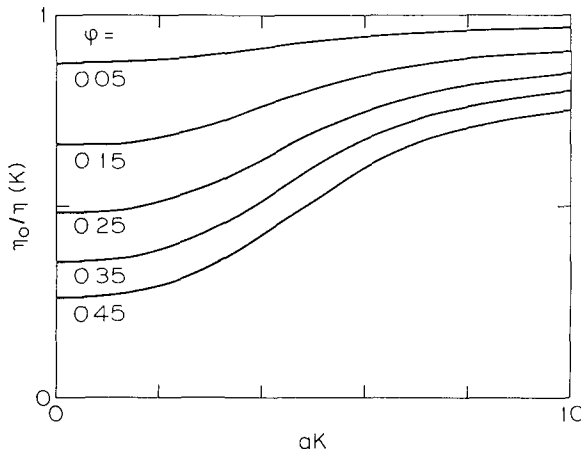


Fig. 1. Wave vector dependence of $\eta_0/\eta(k)$ for five values of the volume fraction ϕ , as results from eq. (7.8).

viscosity increases monotonically as a function of the wave vector, from its small- k limit

$$\lim_{k \rightarrow 0} \lambda^{(0)}(k) = \frac{1}{\eta_0} (1 + \frac{5}{2} \phi \gamma_0^{(2)}/n_0)^{-1} \quad (7.9)$$

(cf eq (7.3)) to its large- k limit

$$\lim_{k \rightarrow \infty} \lambda^{(0)}(k) = 1/\eta_0, \quad (7.10)$$

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 $S_{\gamma_0}(ak)$ in eq (7.8) by $S_{\gamma_0}^{(5)}(ak)$, defined in eq (7.6) It has been checked that repeating the calculations to one lower order (approximating S_{γ_0} by $S_{\gamma_0}^{(4)}$) would not change the results by more than 6%, over the whole range of wave vectors and densities For not too large wave vectors ($ak \leq 3$) 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 wave vectors

Using the fact that $\mathbf{T}_{\gamma_0}^{(n,m)}(\mathbf{k})$ is of order k^{n+m-4} for small k (which follows from eqs (3.8) 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 $k \rightarrow 0$, giving

$$\lim_{k \rightarrow 0} \lambda^{(2)}(k)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) = \lim_{k \rightarrow 0} (6\pi\eta_0 a)^{-1} (\gamma_0^{(2)})^2 k^2 \mathbf{T}_{\gamma_0}^{(1,2)}(\mathbf{k}) \mathbf{B}^{(2,2)^{-1}} \left(\int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{A}_{\gamma_0}^{(2,2)}(\mathbf{r}) [g(\mathbf{r}) - 1] \right) \mathbf{B}^{(2,2)^{-1}} \mathbf{T}_{\gamma_0}^{(2,1)}(\mathbf{k}), \quad (7.11)$$

or explicitly

$$\lambda^{(2)}(k=0) = 20a^4 \eta_0^{-1} (\gamma_0^{(2)})^2 (1 + \frac{5}{2} \phi \gamma_0^{(2)}/n_0)^{-2} \int_0^\infty dq J_1^2(aq) [1 + \phi S_{\gamma_0}(aq)]^{-1} \nu(q) \quad (7.12)$$

In this last equation use has also been made of expression (7.2) for $\mathbf{A}_{\gamma_0}^{(2,2)}(\mathbf{r})^*$

* Note that if expression (7.2) is substituted into eq (7.11) one may replace the connector field $\mathbf{A}^{(2,2)}(\mathbf{r})$ in this expression by $\mathbf{A}^{(2,2)}(\mathbf{r})$ since these two connector fields differ by a finite amount in a single point only (cf eq (4.9))

TABLE I
The expansion in correlation functions (eq (6.12)) of $\lambda(k) \equiv 1/\eta(k)$ for $k=0$, as given by eqs (7.9) and (7.12) to second order

ϕ	$\eta_0\lambda^{(0)}(k=0) + \eta_0\lambda^{(2)}(k=0) = \eta_0\lambda(k=0)$		
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

We have furthermore defined

$$\nu(k) \equiv \int dr e^{ik \cdot r} [g(r) - 1] \tag{7.13}$$

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 Thiele²³⁾ (an explicit analytic expression for $\nu(k)$ is given in ref. 24). The integral on the r.h.s. of eq (7.12) was then computed numerically* (with the approximation of S_{γ_0} by $S_{\gamma_0}^{(5)}$, cf. eq (7.6)). Results are given in table I

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

$$\lim_{k \rightarrow \infty} \lambda^{(2)}(k) = 0, \tag{7.14}$$

as follows from eqs. (3.8), (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 $k \rightarrow \infty$).

8. Discussion

We have calculated the wave vector dependent effective viscosity $\eta(k)$ of a suspension of spherical particles. This quantity relates the Fourier transforms

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

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

$$2\pi/\tau_C \ll \omega \ll a^{-2}\eta_0/\rho_0 \quad (8.1)$$

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 $a^{-2}\eta_0/\rho_0$ is 4×10^6 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^{25,26}). 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 27). 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^{25,26}).

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 so-called fluctuation expansion). The zeroth order result (7.8) 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 wave vector we have evaluated moreover the next non-vanishing term in the fluctuation expansion (given by eq (7.12)), which is of second order and is due to correlations between pairs of spheres. Results for

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

$$\eta^{\text{eff}} \equiv \lim_{k \rightarrow 0} \eta(k) \tag{8.2}$$

to this order are given in table I.

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

The first formula

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi(1 - \phi)^{-1} \tag{8.3}$$

can be obtained by completely neglecting correlations between the spheres, cf. appendix C. 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 Saitô²⁸⁾ (cf. also the derivations in refs. 5, 6, 12 and 29).

The second formula

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi(1 - \frac{5}{2}\phi)^{-1} \tag{8.4}$$

takes into account the same class of self-correlations which contributes to our zeroth order result (7.9) for η^{eff} . However, to arrive at eq. (8.4) these con-

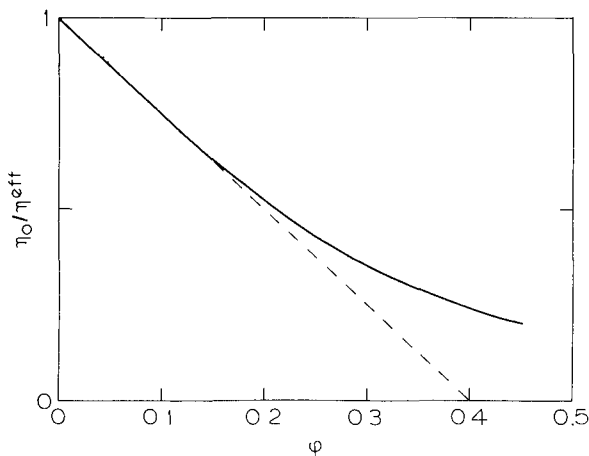


Fig. 2. Volume fraction dependence of the reciprocal of the effective viscosity at zero wave vector. The solid line is taken from table I, dotted and dashed lines from eqs. (8.3) and (8.4), respectively.

tributions are evaluated by an approximation of the hydrodynamic interactions between the spheres which in a way neglects their finite size, cf appendix C. Whereas this so-called 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 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 Lundgren¹⁴⁾ and more recently by several authors^{11,12,13)}. 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_0 . 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 Adelman¹⁰⁾. 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).

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 Saunders³³⁾ and by Krieger and coworkers³⁴⁾ for suspended spherical polystyrene latex particles. The radii of these particles were of the order of 0.1μ , with a narrow size-distribution. Also shown are the data of Kops-Werkhoven and Fijnaut³⁵⁾ for silica spheres of radius 0.07μ . If one compares these experimental results with the calculated values from table I (also plotted in fig. 3) one finds good agreement for volume fractions $\phi \leq 0.2$. At higher concentrations, however,

* 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 Bedeaux³⁰⁾ (for a regular array of freely moving spheres) and by Muthukumar³¹⁾ (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. 32).

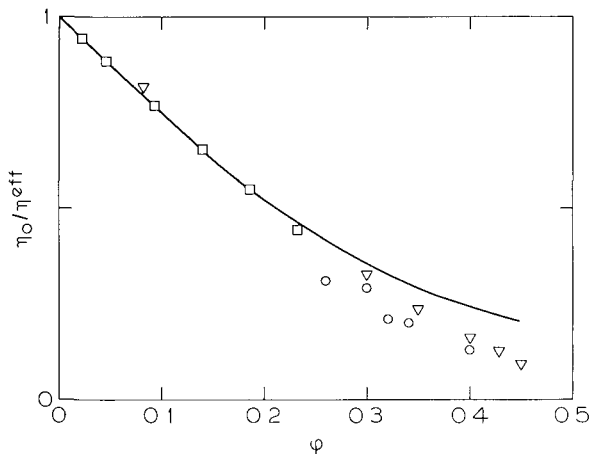


Fig 3 Volume fraction dependence of η_0/η^{eff} The solid line is taken from table I The measured data are from refs 33 (squares) 34 (triangles) and 35 (circles)

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

First, 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 $\sim 20\%$ of the zeroth order result at the highest volume fractions considered (cf table I)

Second, 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 $\eta^{\text{eff}*}$ 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 wave vector dependent

* 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 (2²⁵26)

effective viscosity $\eta(k)$ of a suspension obtained in this paper, with those of the wave vector dependent diffusion coefficient $D(k)$ of the suspended spheres, obtained in ref. 17. The latter quantity is given by

$$D(k) = k_B T [NG(k)]^{-1} \sum_{i,j=1}^N \langle \hat{k} \cdot \boldsymbol{\mu}_{ij} \cdot \hat{k} e^{i\mathbf{k} \cdot \mathbf{R}_{ij}} \rangle, \quad (9.1)$$

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. 27). In this equation $G(k)$ is the static structure factor, $\boldsymbol{\mu}_{ij}$ the mobility tensor and k_B and T denote Boltzmann's constant and the temperature, respectively. The large wave vector limit of $D(k)$ is the self-diffusion coefficient D_s , given by

$$D_s \mathbf{1} = k_B T N^{-1} \sum_{i=1}^N \langle \boldsymbol{\mu}_i \rangle. \quad (9.2)$$

In ref. 17 $D(k)$ has been evaluated through an expansion in correlation functions of higher and higher order. The lowest order term in this expansion is given by eq. (9.1) – with $\boldsymbol{\mu}_{ij}$ replaced by the *effective* pair mobility $\boldsymbol{\mu}_{ij}^{\text{eff}}$,

$$\boldsymbol{\mu}_{ij}^{\text{eff}} \equiv (2\pi)^{-3} \int d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}_{ij}} \mathbf{A}^{(1,1)}(\mathbf{k}) (6\pi a)^{-1} \lambda^{(0)}(k), \quad (9.3)$$

where the tensor $\mathbf{A}^{(1,1)}(\mathbf{k})$ has been defined in eq. (3.6); $\lambda^{(0)}(k)$ (defined in eq. (7.8)) is the zeroth order term in the expansion in correlation functions of the reciprocal of $\eta(k)$. Through the above equations 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 (9.2) of D_s may be replaced by expression (9.3) and one finds

$$D_s = k_B T \frac{1}{3} \pi^{-2} \int_0^{\infty} dk \left(\frac{\sin ak}{ak} \right)^2 \lambda^{(0)}(k). \quad (9.4)$$

Since the largest contribution to the integral in eq. (9.4) arises from the interval $0 < k \leq 1/a$ (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

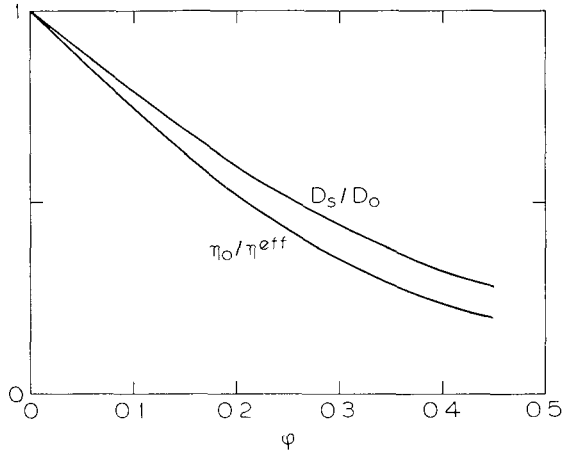


Fig. 4. Volume fraction dependence of the reciprocal of the effective viscosity at zero wave vector η^{eff} (from table I) and of the self-diffusion coefficient (from table III of ref. 17).

in the expansion in correlation functions). Upon integration one then finds

$$D_s \approx k_B T (6\pi\eta^{eff}a)^{-1}. \quad (9.5)$$

In fig. 4 we show the volume fraction dependence of D_s/D_0 (where $D_0 \equiv k_B T (6\pi\eta_0 a)^{-1}$) and η_0/η^{eff} , resulting from an evaluation of the expansion in correlation functions for each of these quantities to second order (cf. ref. 17). One sees that both quantities have a similar concentration dependence, in agreement with eq. (9.5). Deviations from this relation are due to: (i) certain contributions from correlations; (ii) wave vector dependence of the effective viscosity (a consequence of the 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 $\tau \gg \tau_C$ ^{35,36}: 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 (9.5).

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Appendix A

Elimination of the induced forces

According to eqs. (7.2) and (7.3) of the paper by Mazur and van Saarloos¹⁵), one has for the irreducible multipole moments of the induced forces on the spheres the following hierarchy of equations* ($i = 1, 2, \dots, N$),

$$\begin{aligned} \mathbf{F}_i^{(p)} = & 6\pi\eta_0 a (2p-1)!! \mathbf{B}^{(p,p)^{-1}} \odot \overline{\hat{\mathbf{n}}_i^{p-1}} \mathbf{v}_0 \\ & + \sum_{m=2}^{\infty} \sum_{\substack{N \\ j=1 \\ j \neq i}} \mathbf{B}^{(p,p)^{-1}} \odot \mathbf{A}_j^{(p,m)} \odot \mathbf{F}_j^{(m)} \quad (p \geq 2). \end{aligned} \quad (\text{A.1})$$

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

$$\overline{\hat{\mathbf{n}}_i^m} \mathbf{v}_0 \equiv (4\pi a^2)^{-1} a^{-m} \int d\mathbf{r} \overline{(\mathbf{r} - \mathbf{R}_i)^m} \mathbf{v}_0(\mathbf{r}) \delta(|\mathbf{r} - \mathbf{R}_i| - a). \quad (\text{A.2})$$

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

$$\mathbf{v}_0(\mathbf{k}) \equiv (\eta_0 k^2)^{-1} (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \mathbf{F}^{\text{ext}}(\mathbf{k}). \quad (\text{A.3})$$

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

$$\mathbf{F}_i^{(p)} = 6\pi\eta_0 a \sum_{m=2}^{\infty} \sum_{j=1}^N (2m-1)!! \zeta_y^{(p,m)} \odot \overline{\hat{\mathbf{n}}_j^{m-1}} \mathbf{v}_0 \quad (p \geq 2), \quad (\text{A.4})$$

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

* The tensor $\mathbf{B}^{(2,2)^{-1}}$ used here corresponds to $\mathbf{B}^{(2s,2s)^{-1}}$ in ref. 15. Note furthermore that (in view of eq. (2.4)) both the first moments and the antisymmetric parts of the second moments of the induced forces are zero and consequently do not appear in eq. (A.1)

The transverse part of the induced force is given in terms of the moments considered above by the expansion (cf. ref. 15, eq. (3.14))

$$(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \mathbf{F}_i^{\text{ind}}(\mathbf{k}) = \sum_{p=2}^{\infty} (2p-1)!! i^{1-p} j_{p-1}(ak) (\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \widehat{\mathbf{k}}^{p-1} \odot \mathbf{F}_i^{(p)}. \quad (\text{A.5})$$

For the surface moments of the unperturbed flow, furthermore, we have the identity (ref. 15, eq. (4.1))*

$$\widehat{\mathbf{n}}_i^p v_0^S = (2\pi)^{-3} i^p \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}_i} j_p(ak) \widehat{\mathbf{k}}^p v_0(\mathbf{k}). \quad (\text{A.6})$$

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

$$\begin{aligned} 6\pi\eta_0 a \mathbf{v}(\mathbf{k}) &= \mathbf{T}^{(1,1)}(\mathbf{k}) \cdot \mathbf{F}^{\text{ext}}(\mathbf{k}) + \sum_{i,j=1}^N \sum_{n,m=2}^{\infty} e^{-i\mathbf{k}\cdot\mathbf{R}_i} \mathbf{T}^{(1,n)}(\mathbf{k}) \\ &\odot \zeta_{ij}^{(n,m)} \odot (2\pi)^{-3} \int d\mathbf{k}' e^{i\mathbf{k}'\cdot\mathbf{R}_j} \mathbf{T}^{(m,1)}(\mathbf{k}') \cdot \mathbf{F}^{\text{ext}}(\mathbf{k}'), \end{aligned} \quad (\text{A.7})$$

with the tensor field \mathbf{T} defined in eq. (3.8). This equation implies for the kernel \mathbf{M} , defined in eq. (2.8), the expression (3.1).

Appendix B

Proof of eq. (6.8)

We start from the identity

$$\mathcal{H}(1 - nQ\mathcal{B}^{-1}\mathcal{H})^{-1} = \mathcal{H}_{\gamma_0}[1 - (n - \gamma_0)Q\mathcal{B}^{-1}\mathcal{H}_{\gamma_0}]^{-1}, \quad (\text{B.1})$$

where \mathcal{H}_{γ_0} has been defined in eq. (6.2). It is convenient to define an operator I with kernel

$$I(\mathbf{r}|\mathbf{r}') = \begin{cases} 1 & \text{if } \mathbf{r} = \mathbf{r}', \\ 0 & \text{if } \mathbf{r} \neq \mathbf{r}', \end{cases} \quad (\text{B.2})$$

*Note that, with respect to the formulae in ref. 15, we have made the substitution³⁷⁾
 $\frac{\partial^p}{\partial \mathbf{k}^p} k^{-1} \sin k = (-1)^p j_p(k) \widehat{\mathbf{k}}^p$

and a matrix \mathcal{B}_{γ_0} with elements

$$\{\mathcal{B}_{\gamma_0}\}_{n,m} = \begin{cases} \mathbf{A}_{\gamma_0}^{(n,n)}(\mathbf{r} = 0) & \text{if } n = m \neq 1, \\ 0 & \text{elsewise.} \end{cases} \quad (\text{B.3})$$

With these notations we can write

$$\mathcal{H}_{\gamma_0} = \overset{\circ}{\mathcal{H}}_{\gamma_0} + \mathcal{B}_{\gamma_0} I, \quad (\text{B.4})$$

where $\overset{\circ}{\mathcal{H}}_{\gamma_0}$ is defined in eq. (6.9). In the same compact notation we have for the renormalized density

$$\gamma Q = n(1 - Q\mathcal{B}^{-1}\mathcal{B}_{\gamma_0})^{-1}Q, \quad (\text{B.5})$$

cf. eqs. (6.4) and (6.7).

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

$$\mathcal{H}_{\gamma_0} = \mathcal{H}_{\gamma_0} (1 - \gamma_0 Q\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}. \quad (\text{B.6})$$

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

$$\begin{aligned} \mathcal{H}(1 - nQ\mathcal{B}^{-1}\mathcal{H})^{-1} &= \mathcal{H}_{\gamma_0}(1 - nQ\mathcal{B}^{-1}\mathcal{H}_{\gamma_0} + \gamma_0 Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0})^{-1} \\ &= \mathcal{H}_{\gamma_0}(1 - (1 - nQ\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}(n - \gamma_0)Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0})^{-1}(1 - nQ\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}. \end{aligned} \quad (\text{B.7})$$

We now use the identity

$$(1 - nQ\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}\gamma_0 Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0} = \gamma_0 Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0}, \quad (\text{B.8})$$

which follows from $I\overset{\circ}{\mathcal{H}}_{\gamma_0} = 0$, and another identity

$$(1 - nQ\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}nQ = n(1 - Q\mathcal{B}^{-1}\mathcal{B}_{\gamma_0})^{-1}Q \equiv \gamma Q \quad (\text{B.9})$$

(cf. eq. (B.5)). Eq. (B.9) is a consequence of the fact that $nIn = n$.

Substituting eqs. (B.8) and (B.9) into eq. (B.7), one then finds for the 1,1 element of this matrix

$$\begin{aligned} \{\mathcal{H}(1 - nQ\mathcal{B}^{-1}\mathcal{H})^{-1}\}_{1,1} &= \{\mathcal{H}_{\gamma_0}(1 - \delta\gamma Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0})^{-1}(1 - nQ\mathcal{B}^{-1}\mathcal{B}_{\gamma_0} I)^{-1}\}_{1,1} \\ &= \{\mathcal{H}_{\gamma_0}(1 - \delta\gamma Q\mathcal{B}^{-1}\overset{\circ}{\mathcal{H}}_{\gamma_0})^{-1}\}_{1,1}. \end{aligned} \quad (\text{B.10})$$

This is the required identity (6.8). A similar identity was used in ref. 17 (eq. (3.7)).

Appendix C

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 wave vector effective viscosity η^{eff} , we first redefine the connector field $\mathbf{A}^{(2,2)}(\mathbf{r})$ in the following way,

$$\mathbf{A}_0^{(2,2)}(\mathbf{r}) \equiv \mathbf{A}^{(2,2)}(\mathbf{r})g_0(r), \quad (\text{C.1})$$

where the function $g_0(r)$ was defined in eq. (5.12). Note that, since $\mathbf{A}_0(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ are identical for $r > 2a$, we may replace the latter field by the former in definition (3.4) of the connector \mathbf{A}_{ij} .

Next consider expression (4.7) for η^{eff} . If we completely neglect correlations, this expression (together with eqs. (3.2) and (3.10)) gives

$$\begin{aligned} (\eta_0/\eta^{\text{eff}} - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) &= -5\phi(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\hat{\mathbf{k}} \\ &: \left[\Delta + \lim_{\varepsilon \rightarrow 0} \sum_{p=1}^{\infty} \left(-\frac{10}{9}n_0\mathbf{A}_0^{(2s,2s)}(\varepsilon\hat{\mathbf{k}}) \right)^p \right] : \hat{\mathbf{k}}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}). \end{aligned} \quad (\text{C.2})$$

Here we have used the fact that $\mathbf{A}^{(n,m)}(\varepsilon\hat{\mathbf{k}})$ is of order ε^{n+m-4} (cf. eq. (3.6)), so that eq. (C.2) does not contain contributions from connectors with upper indices $n + m > 4$. From eqs. (5.10) and (5.15) we see that

$$-\frac{10}{9}n_0 \lim_{\varepsilon \rightarrow 0} \mathbf{A}_0^{(2s,2s)}(\varepsilon\hat{\mathbf{k}}) = \phi(\Delta - 5\Delta : \hat{\mathbf{k}}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\hat{\mathbf{k}} : \Delta), \quad (\text{C.3})$$

and hence

$$\begin{aligned} (\eta_0/\eta^{\text{eff}} - 1)(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) &= -5\phi(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\hat{\mathbf{k}} : [(1 - \phi)\Delta + 5\phi\Delta : \hat{\mathbf{k}}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}})\hat{\mathbf{k}} : \Delta]^{-1} \\ &: \hat{\mathbf{k}}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \\ &= -\frac{5}{2}\phi(1 + \frac{3}{2}\phi)^{-1}(\mathbf{1} - \hat{\mathbf{k}}\hat{\mathbf{k}}). \end{aligned} \quad (\text{C.4})$$

Eq. (C.4) implies that

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi(1 - \phi)^{-1}, \quad (\text{C.5})$$

which is Saitô's formula (8.3).

We remark that, if one would replace the function $g_0(r)$ in eq (C 1) by some other function of 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 $r \leq 2a$ 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 $\mathbf{A}_0^{(2,2)}(\mathbf{r})$ vanishes for $r \leq 2a$. One might expect, therefore, the resulting formula (C 5) to be more accurate than – for instance – a formula which one would obtain by replacing $g_0(r)$ in eq (C 1) by unity for all r . Indeed, in this latter case one finds upon neglecting correlations the result

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi, \quad (\text{C } 6)$$

which is inferior to eq (C 5)

2 Formula (8.4) point-particle approximation

Consider the zeroth order result (7.9) for the effective viscosity at $k = 0$,

$$\eta^{\text{eff}}/\eta_0 = 1 + \frac{5}{2}\phi\gamma_0^{(2)}/n_0, \quad (\text{C } 7)$$

where $\gamma_0^{(2)}$ is given as a function of n_0 through eq (7.5),

$$\gamma_0^{(2)} - \gamma_0^{(2)}\phi \frac{6}{\pi} \int_0^\infty dk j_1^2(k) S_{\gamma_0}(k) [1 + \phi S_{\gamma_0}(k)]^{-1} = n_0 \quad (\text{C } 8)$$

The function $S_{\gamma_0}(k)$ behaves for small k as (cf eq (7.3))

$$S_{\gamma_0}(k) = \frac{5}{2}\gamma_0^{(2)}/n_0 + \mathcal{O}(k^2) \quad (\text{C } 9)$$

If in the integral in eq (C 8) one would approximate this function by its zero- k limit, one would find for $\gamma_0^{(2)}$

$$\gamma_0^{(2)} = n_0(1 - \frac{5}{2}\phi)^{-1}, \quad (\text{C } 10)$$

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

Since the wave vector dependence of the function $S_{\gamma_0}(k)$ which renormalizes the connectors (according to eq (7.2)) 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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