

DIFFUSION OF SPHERES IN A CONCENTRATED SUSPENSION: RESUMMATION OF MANY-BODY HYDRODYNAMIC INTERACTIONS

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We evaluate the wavevector dependent (short-time) diffusion coefficient $D(k)$ for spherical particles in suspension. Our analysis is valid up to high concentrations and fully takes into account the many-body hydrodynamic interactions between an arbitrary number of spheres. By resumming moreover a certain class of correlations, we obtain results which agree well with available experimental data for the small and large wavevector limits of $D(k)$.

1. Recently [1] we evaluated 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 a wavevector dependent diffusion coefficient $D(k)$, which describes the initial decay of the dynamic structurefactor $S(k, t)$ measured by inelastic light or neutron scattering [2]. In our analysis [1] we resummed the hydrodynamic interactions between an arbitrary number of spheres. The importance of these many-body interactions has been demonstrated both theoretically [3] and experimentally [4]. By including at most two-point correlations between the spheres, we obtained in ref. [1] a reasonable agreement with experimental results for D_s [4], for volume fractions $\varphi \lesssim 0.30$. At higher concentrations the calculated values were too large, indicating the importance of higher order correlations.

The extension to ref. [1] presented here is twofold: (i) we extend the formalism to diffusion at arbitrary (non-zero) values of the wavevector; (ii) we resum to all orders the contributions due to a certain class of correlations, the so-called ring-correlations, thereby obtaining results for D_s which agree with the experimental data up to the highest volume fractions.

2. The (short-time) diffusion coefficient $D(k)$ is given by [2]

$$k^2 S(k) D(k) = k_B T N^{-1} \times \sum_{i,j=1}^N \mathbf{k} \mathbf{k} : \langle \boldsymbol{\mu}_{ij} \exp[i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i)] \rangle, \quad (1)$$

in terms of an average of the mobility tensor $\boldsymbol{\mu}_{ij}$ of spheres i and j , which have positions \mathbf{R}_i and \mathbf{R}_j respectively. The mobilities depend on the whole configuration of the N spheres and may be calculated from the linear Stokes equation [5]. Also, $S(k)$ is the static structurefactor and k_B and T denote Boltzmann's constant and the temperature respectively.

Adopting the notation used in ref. [1], we may write ^{#1}

$$S(k) D(k) / D_0 - 1 = -k^{-2} N^{-1} \mathbf{k} \mathbf{k} : P [n A (1 - n Q A)^{-1} n] (\mathbf{k} | \mathbf{k}) P. \quad (2)$$

In eq. (2) an average is taken of the \mathbf{k}, \mathbf{k} element of the integral operator between braces. The propagator A is a matrix of which the elements characterize a hydrodynamic interaction between two induced-force multipoles. The microscopic numberdensity of the spheres is given by n . In \mathbf{r} representation, the elements of A are convolution operators and n is a diagonal operator. The object $P = 1 - Q$ projects out the first multipole moment of an induced force. The Stokes-Einstein value

^{#1} The operator A used in eq. (2) corresponds to $\mathcal{B}^{-1} \mathcal{A}$ in ref. [1].

of the diffusion coefficient is denoted by D_0 . In the limit $k \rightarrow \infty$, eq. (2) reduces to the expression for D_s given in ref. [1].

3. The expression between braces in eq. (2) may be expanded in powers of the density fluctuations $\delta n \equiv n - n_0$, where n_0 is the average numberdensity of the spheres. In ref. [1] we evaluated D_s to second order in this so-called fluctuation expansion. There is however a certain class of contributions due to correlations which may be resummed to all orders. To this end we define for arbitrary γ_0 a renormalized propagator A_{γ_0} by

$$A_{\gamma_0} \equiv A(1 - \gamma_0 Q A)^{-1}. \quad (3)$$

We choose γ_0 to be a function of the concentration n_0 ,

$$\gamma_0 [1 - Q A_{\gamma_0}(\mathbf{r} = 0)] = n_0, \quad (4)$$

where $A_{\gamma_0}(\mathbf{r})$ is the kernel of the operator A_{γ_0} defined above. One may now prove the identity

$$A(1 - n Q A)^{-1} n = A_{\gamma_0}(1 - \delta \gamma Q \hat{A}_{\gamma_0})^{-1} \gamma, \quad (5)$$

where $\gamma \equiv \gamma_0 + \delta \gamma \equiv n \gamma_0 / n_0$ is a renormalized vertex and \hat{A}_{γ_0} is a cut-out propagator with kernel

$$\hat{A}_{\gamma_0}(\mathbf{r}) = A_{\gamma_0}(\mathbf{r}) \quad \text{for } \mathbf{r} \neq 0, \quad \hat{A}_{\gamma_0}(\mathbf{r} = 0) = 0. \quad (6)$$

In ref. [1] we defined a renormalized propagator A_{n_0} according to eq. (3), with γ_0 equal to n_0 , and proved the identity

$$A(1 - n Q A)^{-1} n = A_{n_0}(1 - \delta n Q A_{n_0})^{-1} n, \quad (7)$$

which did not contain a renormalized vertex, nor a cut-out propagator. Both expressions (5) and (7) are equivalent. However, the zeroth order term in the $\delta \gamma$ -expansion differs from the corresponding term in the δn -expansion: the latter contains the full hydrodynamic interactions between an arbitrary number of spheres in the absence of correlations, while the former moreover contains a class of self-correlations. In a diagrammatic representation this class corresponds to ringdiagrams. Through formulae (3) and (4) the resummation of these diagrams is performed algebraically. Furthermore, the contributions of order $(\delta \gamma)^2$ in the $\delta \gamma$ -expansion are much smaller than those of order $(\delta n)^2$ in the fluctuation expansion described in ref. [1]. This indicates that the former expansion converges faster than the latter one. We remark that to linear order in the density γ_0 equals n_0 and both fluctuation expansions are identical.

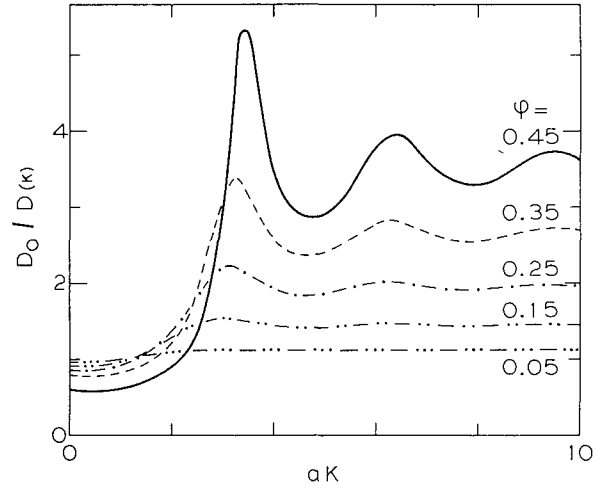


Fig. 1. $D_0/D(k)$ as a function of the wavevector k times the particle radius a , for five values of the volume fraction φ .

4. We have evaluated $D(k)$ given by eq. (2) up to and including terms of second order in $\delta \gamma$, using eq. (5). The pair distributionfunction (necessary for the calculation of $S(k)$ and $\langle(\delta \gamma)^2\rangle$) was approximated by the solution of the Percus–Yevick equation. The resulting wavevector dependence of $D_0/D(k)$ is plotted in fig. 1, for five values of the volume fraction φ [note that in the absence of hydrodynamic interactions $D_0/D(k)$ equals the

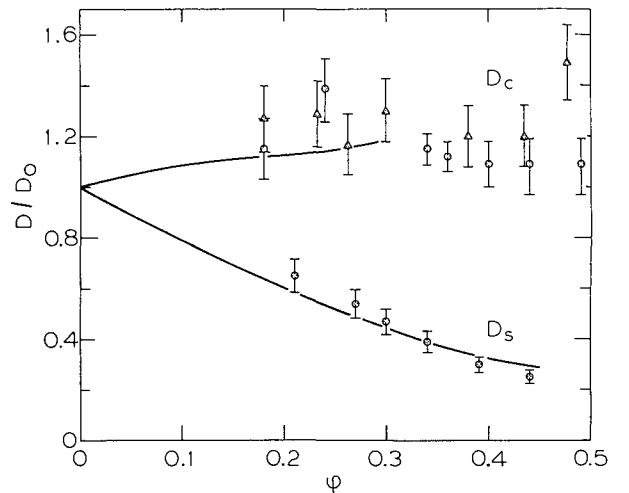


Fig. 2. D_s/D_0 and D_c/D_0 as a function of the volume fraction φ . The solid lines give the results of our calculations. Experimental data for D_s (shown by dots) are from ref. [4]; for D_c , dots are from ref. [6] and triangles from ref. [7].

structurefactor $S(k)$]. In fig. 2 we have plotted the concentration dependence of the two limits

$$D_s = \lim_{k \rightarrow \infty} D(k) \quad \text{and} \quad D_c = \lim_{k \rightarrow 0} D(k), \quad (8)$$

together with experimental results. The theoretical values for the self-diffusion coefficient D_s are given for $\varphi \leq 0.45$, while the values for the collective diffusion coefficient D_c are only shown for $\varphi \leq 0.30$. At higher concentrations the calculated values for D_c become less and less reliable due to cancellations.

For D_s agreement with the experiments of Pusey and van Megen [4] is obtained, up to the highest (experimental) volume fractions. The experimental data [6,7] for D_c indicate that this quantity is rather insensitive to changes in the concentration over a large range of volume fractions; a remarkable result, which is confirmed by our calculations.

Details of this work will be given elsewhere.

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