

Diffusion and light scattering in dispersions of charged particles with thin electrical double layers

D.N. Petsev^a, N.D. Denkov^a and K. Nagayama^b

^a *Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, University of Sofia, Faculty of Chemistry, 1126 Sofia, Bulgaria*

^b *Nagayama Protein Array Project, ERATO, JRDC, 5-9-1 Tokodai, Tsukuba 300-26, Japan*

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The perturbation approach of Barker and Henderson is applied to obtain analytical formulae for the collective diffusion coefficient, short-time self-diffusion coefficient, sedimentation velocity, static and dynamic structure factors at low particle concentration. All these quantities are expressed as explicit functions of the system parameters (particle size and charge, electrolyte concentration, Hamaker constant, etc.) and can be easily calculated if the latter are known. By using light scattering experiments information on the particle charge (or potential) and Hamaker constant can be obtained.

1. Introduction

The general approach for studying the diffusion phenomena in suspensions of interacting Brownian particles at low volume fraction was developed by Batchelor [1,2] and Felderhof [3–7]. These authors presented the first-order (with respect to particle concentration) correction terms for the sedimentation and diffusion coefficients of hard spheres as a sum of different contributions. The latter are expressed as integrals over the radial distribution function of the particles.

In order to take into account long-range (e.g. electrostatic) interactions usually numerical computations are needed in order to determine the concentration dependence of both the collective and self-diffusion coefficients [8,9]. Recently, simple analytical expressions for the concentration dependence of the collective and short-time self-diffusion coefficients of charged colloidal particles were derived [10,11]. The sedimentation velocity, static structure factor and wave-dependent diffusion coefficient of diluted dispersions could also be treated in the framework of the same approach [11]. The model is very simple for weakly charged particles and is in good agreement with the experimental results [10]. The case of strongly charged particles is more complex but

it can be simplified by using a perturbation approach [11]. However, in order to relate the diffusion coefficients to the actual properties of the particles (surface charge and/or potential) one needs to solve numerically the nonlinear Poisson–Boltzmann equation.

In the particular case of thin electrical double layers ($\kappa a > 1$, κ^{-1} is the Debye screening length and a is the particle radius), a simple analytical relation between the particle charge or surface potential and the diffusion coefficient (measured by dynamic light scattering), and the second osmotic virial coefficient (measured by static light scattering) could be established without a numerical solution of the Poisson–Boltzmann equation. This could be achieved by using the asymptotic solution of Chew and Sen [12] for the potential distribution around a charged spherical particle with a thin electrical double layer. Such approach enables one to treat arbitrarily charged particles in the framework of a simple analytical model, if the electrolyte concentration is high enough. However, at thin electrical double layers the van der Waals interaction should also be taken into account.

The derivation of simple formulae for the electrostatic and van der Waals contributions to the concentration dependence of the collective diffusion coefficient of arbitrarily charged particles with thin electrical double layers is the main aim of the present

article. The approach is also applied for calculation of the static structure factor, sedimentation velocity and short-time self-diffusion coefficient. The paper is organized as follows: section 2 reviews briefly the principal concepts used for expressing the diffusion coefficient as a linear function of the particle volume fraction; in section 3 the radial distribution function of the particles is discussed; section 4 is devoted to the derivation of an analytical expression for the electrostatic contribution; section 5 deals with the problem of the van der Waals interactions; section 6 gives some other applications of the approach and section 7 summarizes the conclusions.

2. Concentration dependence of the collective diffusion coefficient D_C

Following the approach of Felderhof [3,4] one can write

$$D_C(\Phi) = D_0(1 + \lambda\Phi), \quad (2.1)$$

where

$$\lambda = \lambda_V + \lambda_O + \lambda_A + \lambda_S + \lambda_D. \quad (2.2)$$

D_C is the collective diffusion coefficient, and D_0 is the diffusion coefficient at volume fraction $\Phi \rightarrow 0$. The latter may differ from the Stokes–Einstein value [13]

$$D_{SE} = \frac{kT}{6\pi\eta a} \quad (2.3)$$

when charged Brownian particles are considered, because of deformation of the counterion atmosphere [10,14–17]. kT is the thermal energy, η the shear viscosity of the solvent and a is the particle radius. The different contributions in eq. (2.2) are presented as integrals over expressions depending on the equilibrium radial distribution function $g(r)$ (see refs. [3,4,18–21]).

3. Radial distribution function

Following the perturbation approach [22] the potential of mean force $W(r)$ and radial distribution function (RDF) $g(r)$ for diluted dispersion of charged particles can be written in the following form (cf. also ref. [11]):

$$W = W^{\text{RHS}} + W^{\text{EL}} + W^{\text{VW}}, \quad (3.1)$$

$$g(r) \approx g_0(r) \left(1 - \frac{W_1(r)}{kT} \right) \\ = \exp\left(-\frac{W^{\text{RHS}}}{kT} \right) \left(1 - \frac{W^{\text{EL}}}{kT} - \frac{W^{\text{VW}}}{kT} \right). \quad (3.2)$$

With g_0 and W^{RHS} we denote the RDF and potential of mean force for the reference hard species (RHS) system, while $W_1(r) < kT$ is the perturbation part which includes the tails ($r > \sigma \geq 2a$) of the electrostatic and/or van der Waals contributions. According to Barker and Henderson [22] one can derive the particle radius a_0 in the RHS system by the expression

$$\frac{a_0}{a} = \int_0^{\tilde{\sigma}} dx [1 - g(x)] \equiv \gamma, \quad (3.3)$$

where a is the actual particle radius, $x = r/2a$ and $\tilde{\sigma} = \sigma/2a$. For diluted dispersions

$$g_0(r) = 0, \quad r < 2a_0, \\ = 1, \quad r \geq 2a_0.$$

Finally, a criterion for establishment of the upper integration limit $\tilde{\sigma}$ should be formulated. As discussed by Barker and Henderson [22] the choice of σ is a matter of convenience (to some extent) if we are interested in the first-order correction only. We use

$$\frac{W(x = \tilde{\sigma})}{kT} = \frac{1}{2}, \quad (3.4)$$

which was found to be rather appropriate for the case of purely repulsive particle interactions [11]. The latter equation defines $\tilde{\sigma}$ as the dimensionless distance at which the interaction energy $W(r)$ equals the Brownian kinetic energy $kT/2$.

By introducing eq. (3.2) into eq. (2.2) we obtain the following expression for the coefficients λ_i ($i = V, O, A, S$):

$$\lambda_i = \lambda_i^{\text{RHS}} + \lambda_i^{\text{ELP}} + \lambda_i^{\text{VW}}. \quad (3.5)$$

The terms λ_i^{RHS} and λ_i^{ELP} (electrostatic perturbation) were discussed in more detail in ref. [11].

For clarity the electrostatic and van der Waals con-

tributions are considered separately below.

4. Diffusion of strongly charged particles with thin electrical double layers

The pair interaction energy between arbitrarily charged colloidal particles (in a superposition approximation) can be expressed in the following form [23] (see also ref. [11]):

$$\frac{W^{\text{EL}}(r)}{kT} = \frac{W_0}{kT} 2a \exp(2\kappa a) \frac{\exp(-\kappa r)}{r}, \quad (4.1)$$

where

$$\frac{W_0}{kT} = \tilde{W}_0 = \frac{e^2 \bar{y}^2 \exp(-2\kappa a)}{2\epsilon k T a}, \quad (4.2)$$

e is the elementary charge, ϵ is the dielectric constant and κ is the screening parameter [23]. The quantity \bar{y} can be obtained by numerical integration of the nonlinear Poisson–Boltzmann equation [11,23]. It is related to the dimensionless potential distribution around the colloidal sphere $y = e\Psi(r)/kT$ by means of the expression [23]

$$y(r) = \frac{e^2}{\epsilon k T} \bar{y} \frac{\exp(-\kappa r)}{r}, \quad \text{for } |y| \ll 1. \quad (4.3)$$

By using the outer asymptotic solution of the Poisson–Boltzmann equation, derived by Chew and Sen [12], one obtains

$$\bar{y} = \frac{4a\epsilon k T}{e^2} \left(t + \frac{1}{2\kappa a} t^3 \right) \exp(\kappa a), \quad (4.4)$$

where

$$t = \tanh(y_s/4), \quad y_s = \frac{e\Psi_s}{kT}, \quad (4.5)$$

Ψ_s is the actual surface potential of the particle. Hence, for \tilde{W}_0 we obtain

$$\tilde{W}_0 = \frac{8\epsilon k T a}{e^2} \left(t + \frac{1}{2\kappa a} t^3 \right)^2. \quad (4.6)$$

The substitution of eq. (4.6) into (4.1) gives the energy of interaction between two colloidal particles with arbitrarily high surface potential y_s and thin electrical double layer ($\kappa a > 1$).

The condition $\kappa a > 1$ enables one to derive also an explicit (although approximate) expression for $\bar{\sigma}$. Let us assume that

$$\bar{\sigma} = 1 + \frac{1}{\kappa a} + \Delta, \quad (4.7)$$

where

$$\Delta \ll 1 + \frac{1}{\kappa a}. \quad (4.8)$$

Combining eqs. (3.4), (4.1), (4.2) and (4.7) and keeping only the leading term one obtains

$$\Delta \approx -\frac{1}{\kappa a} \left[1 + \frac{1}{2} \ln \left(\frac{\kappa a + 1}{2\kappa a \tilde{W}_0} \right) \right]. \quad (4.9)$$

Hence

$$\bar{\sigma} = 1 - \frac{1}{2\kappa a} \ln \left(\frac{\kappa a + 1}{2\kappa a \tilde{W}_0} \right). \quad (4.10)$$

In conclusion, the thin electrical double layer approximation ($\kappa a > 1$) allows: (i) to avoid the numerical calculation of the Poisson–Boltzmann equation by using eq. (4.6); the latter relates \tilde{W}_0 with the surface potential y_s ; (ii) to obtain an explicit expression for $\bar{\sigma}$ instead of solving the transcendental equation (3.4). The RHS radius a_0 , however, should be derived by simple numerical integration of eq. (3.3).

The charge z_0 is related to the surface potential y_s by [12]

$$z_0 = -\frac{2\kappa a \epsilon k T a}{e^2} \left(\sinh(y_s/2) + \frac{2}{\kappa a} \tanh(y_s/4) \right). \quad (4.11)$$

Once the quantities \tilde{W}_0 , $\bar{\sigma}$ and γ are known we may calculate the collective diffusion coefficient D_C (see eqs. (2.1) and (2.2)),

$$D_C = D_0 [1 + (\lambda_V + \lambda_O + \lambda_D + \lambda_A^{\text{RHS}} + \lambda_S^{\text{RHS}}) \Phi], \quad (4.12)$$

where [11] (see also eq. (3.3))

$$\lambda_V = 8\gamma^3 + 2\tilde{W}_0 \exp[2\kappa a(1 - \bar{\sigma})] \frac{3(1 + 2\kappa a \bar{\sigma})}{(\kappa a)^2}, \quad (4.13)$$

$$\lambda_O = -6\gamma^2 - 2\tilde{W}_0 \exp[2\kappa a(1 - \bar{\sigma})] \frac{3}{\kappa a}, \quad (4.14)$$

$$\lambda_A^{\text{RHS}} = -\frac{15}{8\gamma} + \frac{9}{64\gamma^3} + O(\gamma^{-5}), \quad (4.15)$$

$$\lambda_S^{\text{RHS}} = \frac{75}{256\gamma^4} + O(\gamma^{-6}), \quad (4.16)$$

$$\lambda_D = 1. \quad (4.17)$$

The electrostatic contributions λ^{ELP} and λ_V^{ELP} (the terms proportional to \tilde{W}_0 in eqs. (4.12) and (4.13)) are presented in fig. 1 as functions of κa . The parameters used are $a = 10$ nm and $\psi_s = 100$ mV. The exact numerical solutions (the full curves) are in very good agreement with the approximate ones (dashed curves). These electrostatic contributions dominate the remaining counterparts (e.g. hard sphere, or van der Waals – see below) for $\kappa a \leq 5$. For large values of κa , both λ^{ELP} and λ_V^{ELP} tend to zero as expected. The electrostatic contributions in λ_A and λ_S are omitted in eq. (4.12) since they are negligible in comparison with the other terms [11].

5. Contribution of van der Waals interactions to the collective diffusion coefficient D_C

For particles with thin electrical double layers ($\kappa a > 1$) the van der Waals interactions between the particles may become operative. Following the perturbation approach one can obtain expressions for

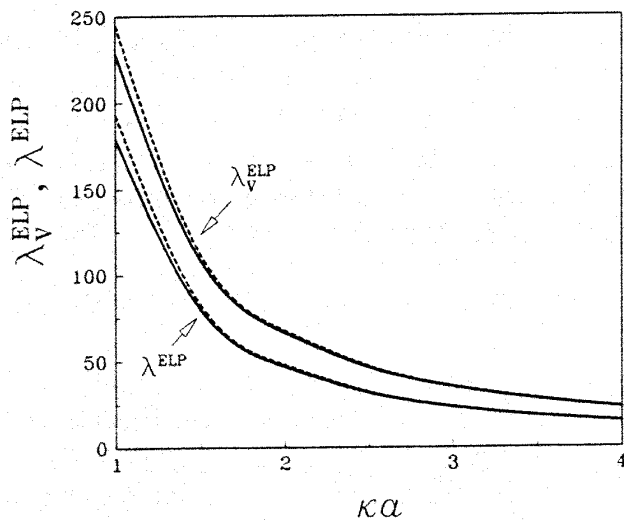


Fig. 1. λ_V^{ELP} and λ^{ELP} versus κa . The full curves present the numerical calculations and the dashed curves correspond to the perturbation model. The parameters used are $a = 10$ nm and $\psi_s = 100$ mV.

their contribution to the collective diffusion coefficient by including the van der Waals interaction energy in eq. (3.2) (see also eq. (3.3)) [8]:

$$W^{\text{vw}} = -\frac{A_H}{6kT} \left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\left(\frac{r^2 - 4a^2}{r^2}\right) \right], \quad (5.1)$$

where A_H is the Hamaker constant. Thus one obtains

$$\lambda_V^{\text{vw}} = \frac{4A_H}{kT} \left[\frac{\tilde{\sigma}}{3} + \frac{\tilde{\sigma}^3}{3} \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) + \frac{1}{12} \ln\left(\frac{\tilde{\sigma} + 1}{\tilde{\sigma} - 1}\right) \right], \quad (5.2)$$

$$\lambda_O^{\text{vw}} = -\frac{A_H}{kT} \left[1 + \left(\tilde{\sigma}^2 - \frac{1}{2}\right) \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) \right], \quad (5.3)$$

$$\lambda_A^{\text{vw}} = \frac{A_H}{6kT} \left\{ \frac{27}{64} \left[\frac{1}{3\tilde{\sigma}^3} \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) + \frac{7}{12} \ln\left(\frac{\tilde{\sigma} + 1}{\tilde{\sigma} - 1}\right) - \frac{7}{6\tilde{\sigma}} - \frac{7}{18\tilde{\sigma}^3} + \frac{1}{10\tilde{\sigma}^5} \right] - \frac{15}{8} \left[\frac{1}{\tilde{\sigma}} \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) + \frac{5}{4} \ln\left(\frac{\tilde{\sigma} + 1}{\tilde{\sigma} - 1}\right) - \frac{5}{2\tilde{\sigma}} + \frac{1}{6\tilde{\sigma}^3} \right] \right\}, \quad (5.4)$$

$$\lambda_S^{\text{vw}} = -\frac{25}{128} \frac{A_H}{kT} \left[\frac{1}{2\tilde{\sigma}^2} + \frac{1}{4\tilde{\sigma}^4} - \frac{1}{12\tilde{\sigma}^6} + \left(\frac{1}{2} - \frac{1}{4\tilde{\sigma}^4}\right) \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) \right]. \quad (5.5)$$

The numerical calculations show that for arbitrary values of $\tilde{\sigma}$ the ratio $(\lambda_A^{\text{vw}} + \lambda_S^{\text{vw}}) / (\lambda_V^{\text{vw}} + \lambda_O^{\text{vw}})$ is less than 0.03. Hence, with high accuracy one can express the van der Waals contribution as

$$\lambda^{\text{vw}} = \frac{A_H}{kT} \left[\frac{4}{3}\tilde{\sigma} - 1 + \left(\frac{4}{3}\tilde{\sigma}^3 - \tilde{\sigma}^2 + \frac{1}{6}\right) \ln\left(\frac{\tilde{\sigma}^2 - 1}{\tilde{\sigma}^2}\right) + \frac{2}{3} \ln\left(\frac{\tilde{\sigma} + 1}{\tilde{\sigma}}\right) \right]. \quad (5.6)$$

One should bear in mind that eq. (4.10) is not appropriate for obtaining $\tilde{\sigma}$ in this case, because the latter was derived assuming only electrostatic interactions between the particles. Hence, for the determination of $\tilde{\sigma}$ one should solve numerically eq. (3.4) with $W(x)$ being the sum of the electrostatic

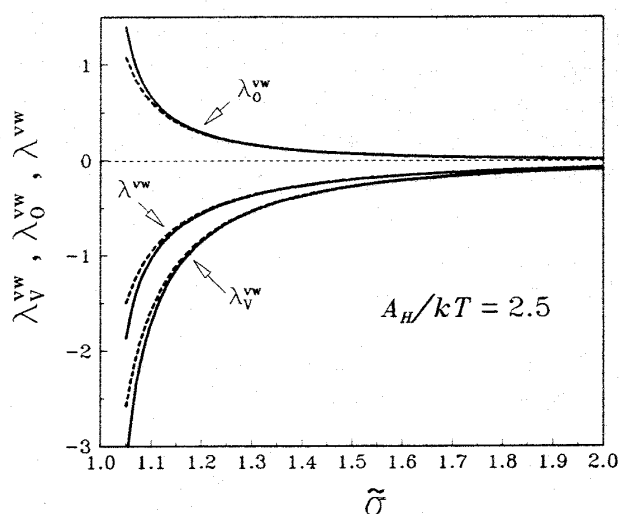


Fig. 2. λ_V^{vw} , λ_O^{vw} and λ_A^{vw} versus $\tilde{\sigma}$. The full curves present the numerical calculations and the dashed curves correspond to the perturbation model. The parameters used are $a=10$ nm and $A_H/kT=2.5$.

and van der Waals interaction energies if both are considered simultaneously.

In fig. 2 the results for λ_V^{vw} , λ_O^{vw} and λ_A^{vw} calculated by means of eqs. (5.2), (5.3) and (5.6) are compared with exact numerical results (see the integrals (2.8) and (2.18) in ref. [4]; the lower limit of integration is taken to be $r=\sigma=2a\tilde{\sigma}$). The Hamaker constant $A_H/kT=2.5$ is used in these calculations. One sees that the agreement is very good down to $\tilde{\sigma}=1.1$. This corresponds approximately to $\kappa a \approx 10$. At thinner electrical layers eq. (5.6) underestimates the magnitude of the van der Waals contribution at this value of the Hamaker constant. The reason is that at very small separations $|W^{\text{vw}}/kT|$ becomes much larger than unity and the approximation eq. (3.2) is not correct.

6. Other applications

The same approach can be applied in a straightforward manner to several other phenomena [11]. The short-time self-diffusion coefficient D_S^S can be calculated by using the known expression [4] (cf. also ref. [11])

$$D_S^S = D_0(1 + \lambda_A \Phi),$$

$$\lambda_A = \lambda_A^{\text{RHS}} + \lambda_A^{\text{ELP}} + \lambda_A^{\text{VW}}. \quad (6.1)$$

Similarly, the sedimentation velocity is given by [11]

$$U = U_0[1 + (\lambda_O + \lambda_A^{\text{RHS}} + \lambda_S^{\text{RHS}} + \lambda_D)\Phi],$$

$$\lambda_O = \lambda_O^{\text{RHS}} + \lambda_O^{\text{ELP}} + \lambda_O^{\text{VW}}, \quad (6.2)$$

where U_0 is the sedimentation velocity of a single colloidal sphere. Again the electrostatic and van der Waals contributions can be neglected in λ_A and λ_S in comparison with these in the λ_O term.

The perturbation approach allows one also to obtain analytical expressions for the angular dependence of the intensity of the scattered light from the suspension (static structure factor $S(q)$) and of the effective diffusion coefficient $D_{\text{EFF}}(q)$ (or the dynamic structure factor) if $(qa)^2 \ll 1$. The magnitude of the scattering vector q is defined as

$$q = \frac{4\pi n}{\lambda} \sin(\Theta/2), \quad (6.3)$$

where n is the refractive index of the solution, λ is the wavelength of the incident beam in vacuo and Θ is the scattering angle. q is typically 10^4 – 10^5 cm^{-1} in light scattering experiments.

Following the approach from ref. [11] one can write

$$S(q) = 1 - \delta_V \Phi, \quad (6.4)$$

$$D_{\text{EFF}}(q) = D_0(1 + \delta \Phi), \quad (6.5)$$

$$\delta = \delta_V + \delta_O + \delta_A + \delta_S + \delta_D, \quad (6.6)$$

where the δ_i ($i=V, O, A, S, D$) are expressed as integrals over the radial distribution function $g(r)$ (see e.g. ref. [24]) and can be presented as

$$\delta_i = \delta_i^{\text{RHS}} + \delta_i^{\text{ELP}} + \delta_i^{\text{VW}}. \quad (6.7)$$

The first two terms, accounting for the reference hard space excluded volume and the electrostatic perturbation, have been calculated previously (see eqs. (5.31)–(5.41)) in ref. [11]). The van der Waals contributions can be expressed in an explicit form for small scattering vectors ($(qa)^2 < 1$),

$$\delta_V^{\text{VW}} = \lambda^{\text{VW}} + \frac{8}{15} \frac{A_H}{kT} (qa)^2 \left[\tilde{\sigma}^3 + \frac{\tilde{\sigma}}{2} + \tilde{\sigma}^5 \ln\left(1 - \frac{1}{\tilde{\sigma}^2}\right) - \frac{1}{4} \ln\left(\frac{\tilde{\sigma}+1}{\tilde{\sigma}-1}\right) \right] + O(q^4 a^4), \quad (6.8)$$

$$\delta_{\text{O}}^{\text{vw}} = \lambda_{\text{O}}^{\text{vw}} - \frac{4}{10} \frac{A_{\text{H}}}{kT} (qa)^2 \left[\tilde{\sigma}^2 + \tilde{\sigma}^4 \ln \left(1 - \frac{1}{\tilde{\sigma}^2} \right) \right] + O(q^4 a^4), \quad (6.9)$$

$$\delta_{\text{D}}^{\text{vw}} = \frac{1}{15} \frac{A_{\text{H}}}{kT} (qa)^2 \left[1 + (\tilde{\sigma}^2 - \frac{1}{2}) \ln \left(1 - \frac{1}{\tilde{\sigma}^2} \right) \right] + O(q^4 a^4), \quad (6.10)$$

$$\delta_{\text{A}}^{\text{vw}} = \lambda_{\text{A}}^{\text{vw}}, \quad (6.11)$$

$$\delta_{\text{S}}^{\text{vw}} = \lambda_{\text{S}}^{\text{vw}} + \frac{15}{256} \frac{A_{\text{H}}}{kT} (qa)^2 \times \left[\left(3 - \frac{2}{\tilde{\sigma}^2} \right) \ln \left(1 - \frac{1}{\tilde{\sigma}^2} \right) + \frac{3}{\tilde{\sigma}^2} - \frac{1}{2\tilde{\sigma}^4} \right] + O(q^4 a^4). \quad (6.12)$$

7. Conclusions

The perturbation approach leads to significant simplification in the consideration of the diffusion and sedimentation in diluted suspensions of charged particles. The thin electric double layer approximation allows one to obtain explicit expressions for the electrostatic and van der Waals contributions. The model enables one to treat charged colloidal particles as lattices, proteins, ionic micelles and microemulsions. It is particularly convenient for interpretation of static and dynamic light scattering data from such systems. The application to other types of interactions (e.g. steric, hydrophobic, etc.) is straightforward.

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References

- [1] G.K. Batchelor, *J. Fluid Mech.* 52 (1972) 245.
- [2] G.K. Batchelor, *J. Fluid Mech.* 74 (1976) 1.
- [3] B.U. Felderhof, *J. Phys. A* 11 (1978) 929.
- [4] B. Cichocki and B.U. Felderhof, *J. Chem. Phys.* 89 (1988) 1049.
- [5] B. Cichocki, B.U. Felderhof and R. Schmitz, *Physico-Chem. Hydrodyn.* 10 (1988) 383.
- [6] M.M. Kops-Werkhoven and H.M. Fijnaut, in: *Light scattering in liquids and macromolecular solutions*, eds. V. Degiorgio, M. Corti and M. Giglio (Plenum Press, New York, 1980).
- [7] J. Neumann, H.L. Swinney, S. Berkowitz and L.A. Day, *Biochemistry* 13 (1974) 4832.
- [8] W.B. Russel, D.A. Saville and W.R. Schowalter, *Colloidal dispersions* (Cambridge Univ. Press, Cambridge, 1989).
- [9] T. Ohtsuki and K. Okano, *J. Chem. Phys.* 94 (1991) 556.
- [10] D.N. Petsev and N.D. Denkov, *J. Colloid Interface Sci.* 149 (1992) 329.
- [11] N.D. Denkov and D.N. Petsev, *Physica A* 183 (1992) 462.
- [12] W.C. Chew and P.N. Sen, *J. Chem. Phys.* 77 (1982) 2042.
- [13] A. Einstein, *Ann. Physik* 17 (1905) 549.
- [14] G.A. Schumacher and T.G.M. van de Ven, *Faraday Discussions Chem. Soc.* 83 (1987) 75.
- [15] G.A. Schumacher and T.G.A.M. van de Ven, *J. Chem. Soc. Faraday Trans.* 87 (1991) 971.
- [16] J.M. Schurr, *Chem. Phys.* 111 (1987) 55.
- [17] M. Medina-Noyola and A. Vizcarra-Rendon, *Phys. Rev. A* 32 (1985) 3596.
- [18] R. Schmitz and B.U. Felderhof, *Physica A* 113 (1982) 907.
- [19] R. Schmitz and B.U. Felderhof, *Physica A* 113 (1982) 103.
- [20] R. Schmitz and B.U. Felderhof, *Physica A* 116 (1982) 163.
- [21] R.B. Jones and R. Schmitz, *Physica A* 149 (1988) 373.
- [22] J.A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.* 23 (1972) 439.
- [23] B. Beresford-Smith, D.Y.C. Chan and D.J. Mitchell, *J. Colloid Interface Sci.* 105 (1985) 216.