

Viscoelasticity and diffusional properties of colloidal model dispersions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S407

(<http://iopscience.iop.org/0953-8984/15/1/356>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 06:25

Please note that [terms and conditions apply](#).

Viscoelasticity and diffusional properties of colloidal model dispersions

Gerhard Nägele

Institut für Festkörperforschung, Teilinstitut Weiche Materie, Forschungszentrum Jülich,
D-52425 Jülich, Germany

E-mail: g.naegele@fz-juelich.de

Received 11 October 2002

Published 16 December 2002

Online at stacks.iop.org/JPhysCM/15/S407

Abstract

We examine linear viscoelastic, and translational and rotational diffusion properties of colloidal model dispersions. Theoretical results are discussed, in comparison with experiments, for monodisperse suspensions of charged and neutral colloidal spheres, and for binary dispersions of differently sized tracer and host particles. The theoretical methods employed comprise a mode-coupling scheme for Brownian particles, and a rooted cluster expansion scheme of tracer diffusion with two- and three-body hydrodynamic interactions included. We analyse in particular the validity of various empirical generalized Stokes–Einstein–Debye (SED) relations between the (dynamic) shear viscosity and translational/rotational diffusion coefficients. Some of these generalized SED relations are basic to microrheological measurements aimed at characterizing the viscoelasticity of complex fluids on the basis of the diffusional properties of immersed tracer particles.

1. Introduction

The translational diffusion coefficient, D_0^t , of a single colloidal sphere of radius a in an unbounded Newtonian solvent with shear viscosity η_0 is given by the familiar Stokes–Einstein (SE) relation, $D_0^t = k_B T / f_0^t$, with friction coefficients $f_0^t = 6\pi\eta_0 a$ and $4\pi\eta_0 a$ for stick and slip boundary conditions, respectively. Likewise, the rotational diffusion coefficient, D_0^r , of an isolated sphere is related to η_0 by the Stokes–Einstein–Debye (SED) relation $D_0^r = k_B T / f_0^r$, with $f_0^r = 8\pi\eta_0 a^3$ in the case of a sticking solvent.

It is of considerable interest to search for generalizations of these single-particle SE(D) relations, which allow one to relate certain diffusional transport properties in concentrated colloidal suspensions to effective suspension viscosities. From a valid generalized SE(D) relation, one can infer a viscoelastic property of the suspension in a non-invasive way and for small sample volumes, by determining the translational or rotational dynamics of a dispersed

tracer particle. Moreover, valid frequency-extended generalized SE(D) relations can be used to determine viscoelastic properties of inhomogeneous (biological) samples using light scattering techniques, for a broad band of fluid strain frequencies not accessible to mechanical rheometers.

For example, the following pair of translational SE relations have been suggested:

$$D_S^t = \frac{k_B T}{6\pi\eta_\infty(\Phi)a_T} \quad (t \ll \tau_I) \quad \text{and} \quad D_L^t = \frac{k_B T}{6\pi\eta(\Phi)a_T} \quad (t \gg \tau_I). \quad (1)$$

Here, the translational short-time and long-time self-diffusion coefficients $D_S^t(\Phi)$ and $D_L^t(\Phi)$ of a tracer sphere with radius a_T are related, respectively, to the high-frequency limiting shear viscosity η_∞ , and to the static shear viscosity η of the host dispersion. The host dispersion consists of colloidal spheres of radius a_H and volume fraction Φ . The particles are subject both to direct interactions (DI), e.g. excluded-volume interactions, and to solvent-mediated hydrodynamic interactions (HI). This makes it necessary to distinguish between short-time ($t \ll \tau_I$) and long-time transport properties ($t \gg \tau_I$), with the structural relaxation time τ_I typically in the millisecond range [1, 2]. Note that D_S^t and η_∞ are both hydrodynamic quantities, while D_L^t and η are long-time transport coefficients of a suspension slightly perturbed from equilibrium by thermal Brownian motion or weak external shear flow. The range of validity of equation (1) has been explored for short and long times mainly for monodisperse systems with a tracer identical to the host spheres (cf, e.g., [3–5]). Very recently, the rotational short-time analogue of equation (1),

$$D_S^r = \frac{k_B T}{8\pi\eta_\infty(\Phi)a_T^3} \quad (t \ll \tau_I^r \approx \tau_I), \quad (2)$$

has also been examined [6–8], where D_S^r is the short-time self-diffusion coefficient of a probe sphere. At first sight, one might expect $D_L^r(\Phi) = k_B T / (8\pi\eta(\Phi)a_T^3)$ to be the long-time SED analogue of equation (2). However, the long-time self-diffusion coefficient of a tracer sphere is defined in a strict sense only for $\lambda = a_T/a_H \gg 1$, when the host suspension behaves as a continuum on the length scale and timescale of the tracer. For $a_T \approx a_H$, a true long-time D_L^r is non-existent, since the rotational scattering function probed by depolarized dynamic light scattering decays then non-exponentially at long times.

An interesting extension of the SE relations in equation (1) to finite strain frequencies ω has been proposed by Mason and Weitz, namely [9]

$$\frac{\eta(s)}{\eta_0} = \frac{D_0^t}{s^2 W(s)}, \quad (3)$$

with $s = i\omega$. This frequency-dependent SE relation relates the dynamic viscosity, $\eta(\omega) = \eta'(\omega) - i\eta''(\omega)$, of the host dispersion, or of a general viscoelastic matrix like a polymer solution, to the Laplace transform, $W(s)$, of the mean squared displacement $W(t) = \langle [r_T(t) - r_T(0)]^2 \rangle / 6$ of the probe sphere. Equation (3) reduces to the short-time and long-time SE relations in equation (1) for $s \rightarrow \infty$ and 0, respectively.

This paper reports on investigations by the author and co-workers on the validity of generalized SE(D) relations, including equations (1)–(3), for suspensions of colloidal spheres. Results are discussed for hard-sphere suspensions, and suspensions of charge-stabilized spheres with a small amount to zero excess electrolytes. The latter systems serve as a representative model for colloidal systems with strong and long-range particle repulsions. In the first part of this work, we examine linear viscoelastic and diffusional properties of monodisperse systems (where $a_T = a_H$), with long-time transport properties determined from a (hydrodynamically rescaled) mode-coupling theory (MCT) [10–12]. The MCT for Brownian particle systems has been established, through comparison with computer simulations and experiment, as a versatile tool for calculating transport coefficients and dynamic scattering

functions in dense systems [5, 13–16]. We show that most of the generalized SE(D) relations are violated to various extents when applied to monodisperse systems. The strongest deviations from SE(D) behaviour are observed for charge-stabilized suspensions. For these systems, the breakdown of the continuum viscoelasticity assumption for the host matrix underlying the SE(D) relations becomes most apparent [17]. However, the description of the host suspension as a continuous viscoelastic medium without local inhomogeneities is expected to be valid when the probe sphere is much larger than the host particles. The Mason–Weitz SE relation, in particular, should be then more reliable as a means for probing the (local) viscoelasticity of the matrix, at least for a limited frequency band. This assertion has been verified by Levine and Lubensky [18] for the special case of a two-fluid model describing the dynamics of a viscoelastic network coupled to a Newtonian solvent.

In this context, it is interesting to identify the conditions for which the continuum behaviour is reached for a binary system of colloidal hard spheres, when the tracer size is progressively enlarged. Therefore, we explore the short-time self-diffusion coefficient of the tracer as a function of tracer-to-host size ratio $\lambda = a_T/a_H$, host concentration Φ , and host viscosity.

2. Long-time diffusion and viscoelasticity

A rigorous starting point for calculating linear viscoelastic properties of colloidal mixtures is provided by the Green–Kubo relation for the dynamic viscosity [12],

$$\eta(\omega) - \eta_\infty = \frac{1}{k_B T V} \int_0^\infty dt e^{-i\omega t} \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle = \frac{1}{k_B T V} \int_0^\infty dt e^{-i\omega t} \Delta\eta(t), \quad (4)$$

with σ_{xy} the microscopic shear stress, V the system volume, and $\Delta\eta$ the stress relaxation function. Equation (4) holds for arbitrary densities, and is used in Stokesian dynamics computer simulations to determine the viscosity in the low-shear limit [19]. Furthermore, it is the starting point for the idealized MCT of linear viscoelasticity. In MCT, the $\eta(\omega)$ of a mixture is approximated in terms of the matrices, $\mathbf{S}(q, t)$ and $\mathbf{S}(q)$, of dynamic and static partial structure factors as [12]

$$\eta(\omega) - \eta_\infty = \frac{k_B T}{6\pi^2} \int_0^\infty dt e^{-i\omega t} \int_0^\infty dq q^4 \text{Tr} \left\{ \left[\frac{d\mathbf{C}}{dq} \cdot \mathbf{S}(q, t) \right]^2 \right\}, \quad (5)$$

with $\mathbf{C}(q) = [\mathbf{1} - \mathbf{S}(q)]^{-1}$. This equation for $\eta(\omega)$ is augmented by MCT equations for $\mathbf{S}(q, t)$, allowing for a self-consistent calculation of diffusional and viscoelastic properties in terms of static quantities [11].

The influence of HI has been neglected in equation (5). An approximate inclusion of far-field HI into idealized MCT has been discussed in [11, 12]. The MCT with far-field HI aims at describing the dynamics of charge-stabilized suspensions in the fluid regime. Many-body HI effects in concentrated suspensions with short-range particle repulsions are accounted for semi-heuristically by multiplying long-time transport coefficients, calculated without HI using MCT, by the corresponding reduced short-time properties with HI included. A rationale of this hydrodynamic rescaling procedure has been given in [5], where it is further explained why hydrodynamic rescaling is not applicable to systems with long-range DI. Figure 1 shows HI-rescaled MCT results for the (reduced) viscosity η , and for reciprocal long-time self-diffusion and collective diffusion coefficients, D_L^t and $D_L^c(q_m)$, of monodisperse colloidal hard spheres, in comparison with experimental data. $D_L^c(q_m)$ quantifies the long-time exponential decay of the dynamic structure factor $S(q, t)$ at a wavenumber q_m related to the extension of the next-neighbour cage around a sphere. $D_L^c(q_m)$ ceases to exist below a certain concentration threshold ($\Phi \approx 0.2$ for hard spheres), where caging effects become so small that $S(q_m, t)$

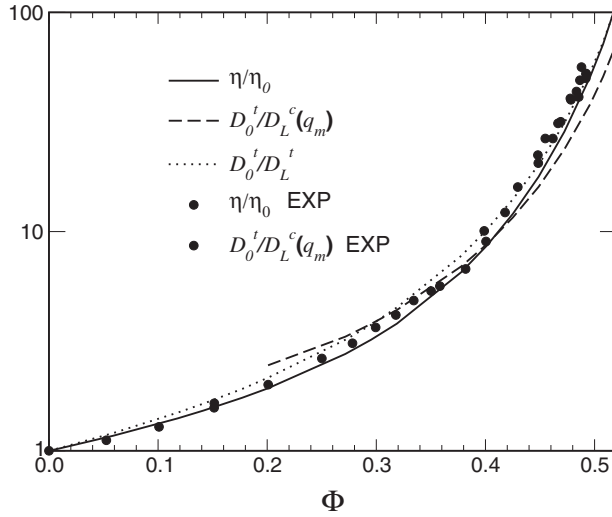


Figure 1. Reduced shear viscosity η/η_0 , reciprocal long-time collective self-diffusion coefficient $D_0^t/D_L^c(q_m)$, and reciprocal long-time self-diffusion coefficient D_0^t/D_L^t for a hard-sphere suspension versus volume fraction Φ . Symbols are experimental data from [20], and the lines are the HI-rescaled MCT predictions [5, 13].

decays non-exponentially [14]. There is good overall agreement between theoretical and experimental data for η and $D_L^c(q_m)$. Moreover, the long-time SE relation in equation (1) is confirmed semi-quantitatively, to the same level of accuracy as the SE relation,

$$D_L^c(q_m) = \frac{k_B T}{6\pi\eta a}, \quad (6)$$

between $D_L^c(q_m)$ and η .

While these SE relations hold reasonably well for hard spheres, a strong violation of the same relations is predicted by MCT for de-ionized, i.e. salt-free, suspensions of highly charged colloidal spheres [5]. Conclusions similar to the ones for the long-time SE relations can be drawn regarding the range of validity of the frequency-dependent SE relation in equation (3). MCT predicts that this relation is valid to a qualitative degree for monodisperse hard spheres, with increasing accuracy at larger volume fractions [5]. Pronounced violations of this relation are found instead for (de-ionized) charge-stabilized suspensions (cf figure 2, left-hand panel). Recently, a modified frequency-dependent SE relation, namely $\Psi_\eta(s) \approx \Psi_W(s)$, has been proposed [5] which relates the normalized dynamic viscosity $\Psi_\eta(s) = (\eta(s) - \eta_\infty)/(\eta - \eta_\infty)$ to $\Psi_W(s) = [1/(s^2 W(s)) - 1/D_S^t]/[1/D_L^t - 1/D_S^t]$. This modified SE relation refers to the reduced frequency dependences of $\eta(s)$ and $W(s)$ only. According to MCT, it should apply more quantitatively than equation (3), and also for the case of charge-stabilized suspensions (see figure 2, right-hand panel). To date, this frequency-dependent SE relation has not been tested experimentally.

3. Short-time SE(D) relations for monodisperse systems

For a test of the SE(D) relations for D_S^t and D_S^r in equations (1) and (2), we plot $H_S^a \eta_\infty/\eta_0$ versus Φ , with $H_S^a = D_S^a/D_0^a$ and $a \in \{t, r\}$. Figure 3, left-hand panel, summarizes theoretical and experimental hard-sphere results for $H_S^a \eta_\infty/\eta_0$, with η_∞ determined from the semi-empirical

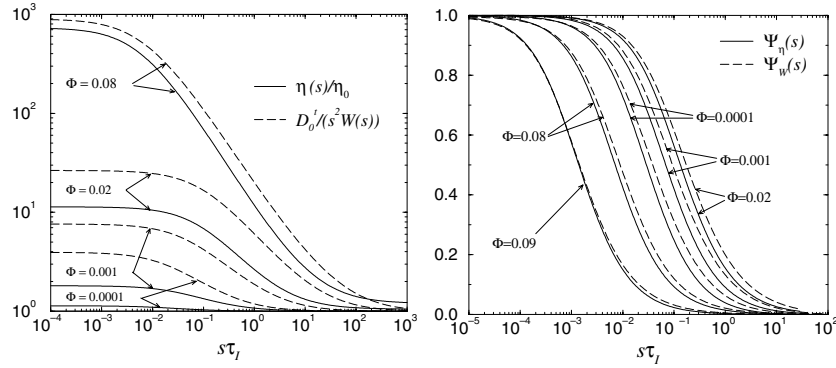


Figure 2. Left: the MCT-calculated dynamic viscosity $\eta(s)/\eta_0$ and $D_0^a/(s^2W(s))$, for de-ionized charge-stabilized suspensions at various values of Φ . Right: the corresponding MCT results for $\Psi_\eta(s)$ and $\Psi_D(s)$ versus $s\tau_l$, with $\tau_l = a^2/D_0^a$. (From [5].)

expression [24]

$$\eta_\infty/\eta_0 = [1 + 1.5\Phi(1 + \Phi - 0.189\Phi^2)]/[1 - \Phi(1 + \Phi - 0.189\Phi^2)]. \quad (7)$$

This expression agrees well with known experimental data for hard spheres up to random close packing, $\Phi \approx 0.64$, where η_∞ diverges. For H_S^t and H_S^r we use the semi-empirical expression $H_S^t = (1 - 1.56\Phi)(1 - 0.27\Phi)$ proposed in [24], and the second-order virial result $H_S^r = 1 - 0.631\Phi - 0.726\Phi^2$ derived in [25]. There is good agreement between experimental and theoretical values for H_S^a . As seen, both short-time SE(D) relations are disobeyed for finite Φ , with larger deviations for rotational diffusion. Figure 3, left-hand panel, examines further the short-time analogue, $D_S^c(q_m) = k_B T / (6\pi\eta_\infty(\Phi)a)$, of equation (6), where η_∞ is related to the short-time collective diffusion coefficient $D_S^c(q_m) = D_0^a H(q_m)/S(q_m)$. The hydrodynamic function $H(q_m)$ of hard spheres and $S(q_m)$ are well described by $H(q_m) = 1 - 1.35\Phi$ and $S(q_m) = 1 + 0.644\Phi(1 - 0.5\Phi)/(1 - \Phi)^3$, respectively, up to $\phi = 0.5$ [14, 15]. The SE relation for $D_S^c(q_m)$ is seen to be more accurate than the SE(D) relations for H_S^a .

Consider next figure 3, right-hand panel, regarding the performance of the short-time SE(D) relations when applied to semi-dilute and de-ionized charge-stabilized systems. As predicted by theory and confirmed subsequently by experiment and computer simulations (see, e.g., [1, 2]), the self-diffusion coefficients of these systems exhibit non-linear Φ -dependences,

$$H_S^a = 1 - A_a\Phi^{E_a}, \quad (8)$$

with amplitudes $A_r \approx 1.3$, $A_t \approx 2.5$ and exponents $E_r = 2$, $E_t = 4/3$. The theoretical curve for $D_S^c(q_m)$, plotted in figure 3, right-hand panel, has been calculated using $H(q_m) = 1 + A_c\Phi^{0.4}$, with $A_c = 1.5$, and $S(q_m)$ determined from the rescaled mean-spherical approximation [1]. The non-linear density dependence of the short-time transport coefficients for de-ionized suspensions originates from the $\Phi^{-1/3}$ scaling of the mean cage radius $r_m = 2\pi/q_m$ [1]. We approximate the short-time viscosity of highly charged spheres, for $\Phi \leq 0.1$, by the leading-order virial form $\eta_\infty/\eta_0 \approx 1 + 2.5\Phi(1 + \Phi)$. According to figure 3, right-hand panel, deviations from $H_S^a\eta_\infty/\eta_0 = 1$ are similarly pronounced to those for hard spheres. In contrast to the hard-sphere case, however, the SE relation for $D_S^c(q_m)$ is clearly violated for charged spheres. The failure of the SE(D) relations for charge-stabilized systems is thus observed both for long and short times.

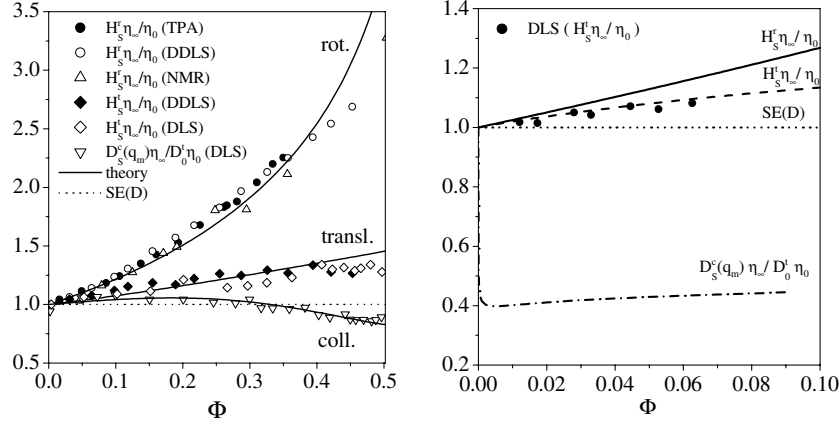


Figure 3. Left: a test of the validity of the short-time SE(D) relations $H_S^a \eta_\infty / \eta_0 = 1$ and $D_S^c(q_m) \eta_\infty / (D_0^c \eta_0) = 1$, with η_∞ from (7). The lines are the theoretical predictions. The symbols are experimental data measured using TPA [6], DDLS [21], NMR [22], and (D)DLS for H_S^t [21] and $D_S^c(q_m)$ [23]. Right: a corresponding test for typical de-ionized charge-stabilized suspensions. (Reproduced from [8].)

4. Tracer dynamics in host suspensions

With increasing $\lambda = a_T/a_H$, the tracer experiences the host suspension more and more as an unstructured continuum, characterized by its macroscopic viscosity. To investigate the approach towards the continuum limit, we have calculated the (reduced) short-time translational/rotational self-diffusion coefficients of an infinitely dilute tracer species,

$$H_S^a(\lambda, \Phi) = 1 + h_{1S}^a(\lambda)\Phi + h_{2S}^a(\lambda)\Phi^2, \quad (9)$$

immersed in a host suspension of colloidal hard spheres, to quadratic order in the host volume fraction Φ . Results for the first and second virial coefficients, $h_{1S}^a(\lambda)$ and $h_{2S}^a(\lambda)$, are obtained from a rooted cluster expansion, with two-body and leading-order three-body HI included [6, 7]. Numerical results for $H_S^t \eta_\infty / \eta_0$ versus Φ , with η_∞ from equation (7), are displayed in figure 4, left-hand panel, for various values of λ . Notice the rather slow convergence towards the SED behaviour, with increasing λ , for the semi-dilute host dispersions under consideration. For all λ considered, the first virial coefficient is well represented by

$$h_{1S}^a = -\frac{2.5}{1 + c_S^a \lambda^{-1}}, \quad (10)$$

with $c_S^r = 3.0$ and $c_S^t = 0.366$ [7].

Figure 4, right-hand panel, shows $D_S^a \approx D_0^a [1 + h_{1S}^a(\lambda)\Phi]$ versus λ , for fixed $\Phi = 0.1$. It nicely illustrates the monotonic decline of the translational/rotational tracer coefficients, from $D_S^a = D_0^a$ at $\lambda = 0$ towards $D_S^a = D_0^a(1 - 2.5\Phi) + \mathcal{O}(\Phi^2)$ for $\lambda \rightarrow \infty$. The large- λ limit is $k_B T / (6\pi\eta_\infty a_T)$ for $a = t$ and $k_B T / (8\pi\eta_\infty a_T^3)$ for $a = r$, with $\eta_\infty / \eta_0 = 1 + 2.5\Phi + 5\Phi^2 + \mathcal{O}(\Phi^3)$. For large λ , the tracer thus experiences the host solution as an effective fluid with a shear viscosity, characterized to first order in Φ by the Einstein result. As is seen, rather large values of λ are required in the case of rotational diffusion for practically reaching the continuum limit. According to experiment, however, the continuum behaviour of the long-time rotational tracer diffusion coefficient is reached for smaller λ (i.e. for $\lambda \approx 10$) at larger Φ , due to the stronger many-body HI and DI of the tracer with the denser shell

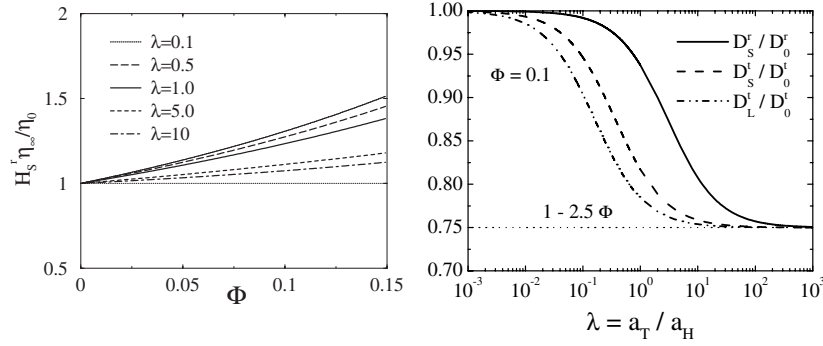


Figure 4. Left: the reduced rotational self-diffusion coefficient H_S^r of the tracer times η_∞/η_0 [7]. The dotted curve represents the generalized SE relation. Right: the reduced translational/rotational short-time self-diffusion coefficients, D_S^t/D_0^t , and reduced translational long-time self-diffusion coefficient, D_L^t/D_0^t , versus λ , for $\Phi = 0.1$.

of surrounding host particles, and memory effects related to caging [8]. In our low-density calculations, near-field lubrication forces and many-body HI contributions beyond the leading-order three-body part have been neglected so far. For $\lambda = 0$, the point-like tracer diffuses for short times in an essentially static environment of host spheres, so its dynamics is affected by the solvent viscosity only. Figure 4, right-hand panel, displays also the long-time self-diffusion coefficient $D_L^t \approx D_0^t[1 + h_{1L}^t \Phi]$ at low Φ , with h_{1L}^t represented to good accuracy by [26]

$$h_{1L}^a = 1 - \frac{2.5}{1 + 0.16\lambda^{-1}}. \quad (11)$$

For all λ , $D_L^t < D_S^t$, consistent with a general rule stating that, due to memory effects, long-time transport coefficients of colloidal systems are always smaller than the corresponding short-time coefficients [1].

Deviations from the SED behaviour of tracer diffusion can be intuitively rationalized by introducing apparent slip–stick parameters, ν , according to [3, 8, 27]

$$\begin{aligned} D_{S,L}^t &= k_B T / [6\pi\eta_0 a_T (1 + \nu_{S,L}^t \Delta\eta)] \\ D_{S,L}^r &= k_B T / [8\pi\eta_0 a_T^3 (1 + \nu_{S,L}^r \Delta\eta)], \end{aligned} \quad (12)$$

with $\Delta\eta$ equal to $\eta/\eta_0 - 1$ and $\eta_\infty/\eta_0 - 1$ for long and short times, respectively. The parameter ν is determined by

$$\nu_{S,L}^a(\lambda, \Phi) = (D_0^a/D_{S,L}^a - 1)/\Delta\eta(\Phi). \quad (13)$$

The friction coefficient has been split here into a part due to the solvent alone, which sticks, and an additional frictional part originating from HI and DI with the host spheres. There is no reason to expect a stick boundary condition, and hence the validity of the non-modified SED relations, for the interaction part. Therefore, $\nu_{S,L}^a$ might range, in principle, from 1 for stick boundary conditions (i.e. for ideal SED behaviour) down to 0 for zero excess friction.

In fact, for a dilute host dispersion of hard spheres one has

$$\nu_{S,L}^a(\lambda, \Phi = 0) = -0.4h_{1S,L}^a(\lambda), \quad (14)$$

with values of $\nu_{S,L}^a$ ranging from 0 for $\lambda = 0$ up to 1 for $\lambda = \infty$. For $\lambda = 1$, $\nu_S^t(1, \Phi = 0) = 0.73$, which is a value rather close to the Φ -averaged slip–stick parameter $\bar{\nu}_S^t = 2/3$. When $\bar{\nu}_S^t$ is used in the modified SE relation, the experimentally determined D_S^t of hard spheres is rather well reproduced up to $\Phi < 0.5$ [8]. The excess frictional part is

thus well described for hard spheres by the perfect slip form $\Delta f_S^t(\phi) = 4\pi(\eta_\infty - \eta_0)a_T$. For rotational diffusion, $v_S^t(1, \Phi = 0) = 0.25$, i.e. a value close to the experimentally determined Φ -averaged slip–stick parameter $\bar{v}_S^t = 0.22$ [8]. The latter value results in a remarkably good description of the experimental H_S^t in figure 3, right-hand panel. Note that \bar{v}_S^t is substantially larger than the value 0 for perfect slip, since the influence of HI is clearly non-negligible at finite host concentrations. For long-time translational diffusion finally, $v_L^t(1, \Phi = 0) = 0.86$. This value of v_L^t is consistent with the semi-quantitative accuracy of the long-time SE relation in equation (1) at $\lambda = 1$.

For de-ionized suspensions of monodisperse charges spheres, MCT predicts that $D_0^t/D_L^t > \eta/\eta_0$ [5], leading to super-stick values of v_L^t larger than one. This implies a breakdown of the continuum picture, thus invalidating the non-modified and the modified long-time SE relations in equations (1) and (12). Due to the long-range electrostatic interactions, a charged tracer sphere experiences particularly strongly the discontinuous nature of its environment.

Acknowledgments

It is a pleasure to thank G H Koenderink, H Zhang, A J Banchio and J Bergenholtz for fruitful collaborations.

References

- [1] Nägele G 1996 *Phys. Rep.* **272** 215–372
- [2] Nägele G, Dhont J K G and Meier G 2002 Diffusion in colloidal and polymeric systems *Diffusion in Condensed Matter* 2nd (revised and enlarged) edn, ed P Heitjans and J Kärger (Berlin: Springer)
- [3] Imhof A, van Blaaderen A, Maret G, Mellema J and Dhont J K G 1994 *J. Chem. Phys.* **100** 2170
- [4] Bergenholtz J, Horn F M, Richtering W, Willenbacher N and Wagner N J 1998 *Phys. Rev. E* **58** R4088
- [5] Banchio A J, Nägele G and Bergenholtz J 1999 *J. Chem. Phys.* **111** 8721
- [6] Koenderink G H, Zhang H, Lettinga M P, Nägele G and Philipse A P 2001 *Phys. Rev. E* **64** 022401
- [7] Zhang H and Nägele G 2002 *J. Chem. Phys.* **117** 5908
- [8] Koenderink G H, Zhang H, Aarts D G A L, Lettinga M P, Philipse A P and Nägele G 2002 *Faraday Discuss.* **123** at press
- [9] Mason T G and Weitz D 1995 *Phys. Rev. Lett.* **74** 1250
- [10] Götze W 1991 *Liquids, Freezing and Glass Transition* ed J-P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
- [11] Nägele G, Bergenholtz J and Dhont J K G 1999 *J. Chem. Phys.* **110** 7037
- [12] Nägele G and Bergenholtz J 1998 *J. Chem. Phys.* **108** 9893
- [13] Banchio A J, Bergenholtz J and Nägele G 1999 *Phys. Rev. Lett.* **82** 1792
- [14] Banchio A J, Nägele G and Bergenholtz J 2000 *J. Chem. Phys.* **113** 3381
- [15] Nägele G, Kollmann M, Pesché R and Banchio A J 2002 *Mol. Phys.* **100** 2921
- [16] Cheng Z, Zhu J, Chaikin P M, Phan S-E and Russel W B 2002 *Phys. Rev. E* **65** 041405
- [17] Soloman M J and Lu Q 2001 *Curr. Opin. Colloid Interface Sci.* **6** 430
- [18] Levine A J and Lubensky T C 2001 *Phys. Rev. E* **63** 041510
- [19] Foss D R and Brady J F 2000 *J. Fluid Mech.* **407** 167
- [20] Segrè P N, Meeker S P, Pusey P N and Poon W C K 1995 *Phys. Rev. Lett.* **75** 958
- [21] Degiorgio V, Piazza R and Jones R B 1995 *Phys. Rev. E* **52** 2707
- [22] Kanetakis J, Tolle A and Sillescu H 1997 *Phys. Rev. E* **55** 3006
- [23] Segrè P N, Behrend O P and Pusey P N 1995 *Phys. Rev. E* **52** 5070
- [24] Lionberger R A and Russel W B 1994 *J. Rheol.* **38** 1885
- [25] Cichocki B, Ekiel-Jezewska M L and Wajnryb E 1999 *J. Chem. Phys.* **111** 3265
- [26] Batchelor G K 1983 *J. Fluid Mech.* **131** 155
Batchelor G K 1983 *J. Fluid Mech.* **137** 467 (corrigendum)
- [27] Lionberger R A 2000 *Advances in Chemical Physics* vol 3, ed I Prigogine and S A Rice (New York: Wiley)