

## Many-Body Hydrodynamic Interactions in Charge-Stabilized Suspensions

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In this joint experimental-theoretical work we study hydrodynamic interaction effects in dense suspensions of charged colloidal spheres. Using x-ray photon correlation spectroscopy we have determined the hydrodynamic function  $H(q)$ , for a varying range of electrosteric repulsion. We show that  $H(q)$  can be quantitatively described by means of a novel Stokesian dynamics simulation method for charged Brownian spheres, and by a modification of a many-body theory developed originally by Beenakker and Mazur. Very importantly, we can explain the behavior of  $H(q)$  for strongly correlated particles without resorting to the controversial concept of hydrodynamic screening, as was attempted in earlier work by Riese *et al.* [Phys. Rev. Lett. **85**, 5460 (2000)].

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Suspensions of colloidal particles undergoing Brownian motion in a low-molecular-weight solvent are ubiquitous in chemical industry, biology, food science, and in medical and cosmetic products. For polar solvents like water, the particles are usually charged. At long to intermediate distances these particles interact electrostatically by an exponentially screened Coulomb repulsion originating from the overlap of the neutralizing electric double layers. A considerable effort has been devoted over the past years to study the dynamics of colloidal model suspensions of charged spheres at the microscopic level [1,2]. The dynamics is determined by a subtle interplay of direct interactions and solvent-flow mediated hydrodynamic interaction (HI). The latter dynamic interaction plays a pivotal role not only in unconfined colloidal systems, but also in microfluidic devices where narrow wall confinements or channels are present [3], and in sedimenting dispersions of large non-Brownian particles [4]. HI in unconfined suspensions is very long ranged. It decays with interparticle distance  $r$  like  $1/r$ . An account of HI effects in theoretical and computer simulation studies is quite challenging due to its many-body nature, which must be accounted for in non-dilute suspensions.

An important measure of the strength of HI with regard to short-time particle diffusion caused by local density gradients is given by the hydrodynamic function [2]

$$H(q) = D_s/D_0 + H_d(q), \quad (1)$$

which is the sum of a wave-number-independent self-part and a  $q$ -dependent distinct part. Here,  $D_s$  is the short-time self-diffusion coefficient, and  $D_0$  is the particle diffusion coefficient at infinite dilution. In the limit of large  $q$ ,  $H(q)$  reduces to  $D_s/D_0$ . Without HI,  $H(q) = 1$  and any variation

in  $H(q)$  is a hallmark of HI. It has a direct physical meaning [5] as the (reduced) mean particle sedimentation velocity for a suspension subject to a weak periodic force field, collinear to the wave vector  $\mathbf{q}$ , and oscillating like  $\cos(\mathbf{q} \cdot \mathbf{r})$ . Experimentally,  $H(q)$  can be determined as a function of wave number through a combination of static and dynamic scattering experiments [6,7].

Experimental findings [6] for the  $H(q)$  of highly charged colloidal spheres at low volume fractions  $\phi$  (typically  $<0.05$ ) are in excellent agreement with theoretical predictions of Nägele *et al.* [2], based on a pairwise-additivity approximation of HI. In its simplest form this theory accounts only for the leading far-field (i.e., Rotne-Prager) part of the hydrodynamic pair mobilities which dominates in dilute systems. The far-field part is pairwise additive and includes terms up to  $\mathcal{O}(1/r^3)$ . The theory necessarily fails for larger densities where many-body HI comes into play. For dense charge-stabilized suspensions with strong many-body HI, the most successful tool to date for calculating  $H(q)$  has been the (zeroth-order)  $\delta\gamma$  method of Beenakker and Mazur [8]. This method accounts approximately for many-body HI through ring diagrams, and it requires the static structure factor  $S(q)$  as the only input. Originally it has been applied to hard-sphere suspensions, where its degree of accuracy for  $H(q)$  has been assessed through comparison with Stokesian dynamics (SD) and Lattice-Boltzmann computer simulations. These comparisons show that it is rather accurate for  $\phi < 0.35$  (cf. discussions below).

In later work, the  $\delta\gamma$  scheme was additionally used to predict the  $H(q)$  for charge-stabilized systems [2,9]. Contrary to hard spheres, no simulation results have been available to date to test its accuracy for charged systems.

Yet it came as a surprise when recent measurements by Riese *et al.* [7] on essentially deionized suspensions of charged silica spheres in the fluid regime at  $\phi = 0.09$ – $0.15$ , revealed  $H(q)$ 's which could not be explained by  $\delta\gamma$  theory: the maximum in  $H(q)$  is much smaller, and the variation in  $q$  much weaker, than theoretically expected. Moreover, and equally surprisingly, the maximum in  $H(q)$  was found to be even smaller than the one for a hard-sphere suspension at equal  $\phi$  [7]. This observation implies that the short-time self-diffusion coefficient of these samples is substantially smaller than the hard-sphere value for the same  $\phi$ . The experimental observation of a stronger hydrodynamic hindrance beyond the hard-sphere prediction was interpreted by these authors as strong evidence for the appearance of hydrodynamic screening in dense (in the sense of strongly correlated) silica-sphere suspensions at low salinity. The  $\delta\gamma$  theory does not include HI screening. To support their assertion, Riese *et al.* fitted  $H(q)$  using a Brinkmann fluid calculation where only the far-field part of the hydrodynamic pair mobility [decaying like  $(\xi/r)^3$ ] is considered. Treating the screening length  $\xi$  as a fitting parameter, they managed to fit their experimental  $H(q)$  [7].

The interpretation of the experiments by Riese *et al.* in terms of hydrodynamic screening caused strong controversy since, on theoretical grounds, there should be no screening of solvent flow in unbounded suspensions of *mobile* spheres [8]. In fact, many-body HI in mobile-sphere suspensions merely leads to an increase in the effective suspension viscosity. Thus, on a coarse-grained level and for distances much larger than typical interparticle distances, only the prefactor of the leading  $1/r$  part in the HI is modified. It must be emphasized that, contrary to nonconfined systems of mobile spheres, hydrodynamic screening is present in systems with spatially fixed obstacles like porous media [10]. In such systems the momentum of flow perturbations is absorbed by fixed obstacles kept in place by external forces. Screening can also occur in the presence of fixed macroscopic boundaries like walls and enclosing pipes. For two parallel walls, HI between two particles in the gap decays asymptotically like  $1/r^2$  for motion parallel to the walls [11]. For cylindrical pipes, HI decays exponentially at distances large compared with the pipe diameter [12]. Furthermore, algebraic screening of fluid flow characterized by a  $1/r^3$  long-distance decay is found in the electrophoresis of colloidal macroions [13].

To date, it had not been possible to explore the apparent failure of  $\delta\gamma$  theory in describing the experiments of Riese *et al.*, since computer simulation studies of dense charge-stabilized systems did not exist so far. The present work includes the first Stokesian dynamics computer simulation study of  $H(q)$  for dense charge-stabilized systems with varying range of electrostatic particle repulsion. The simulations are based on an extension of an accelerated SD code (ASD) for Brownian hard spheres, developed recently by Banchio and Brady [14]. Additionally, since an accurate

experimental determination of  $H(q)$  is quite subtle, with possible sources of error coming, e.g., from an improper assessment of baselines and remnant multiple scattering contributions, we have performed careful x-ray photon correlation spectroscopy (XPCS) measurements of  $H(q)$  and  $S(q)$ , for suspensions of monodisperse fluorinated latex spheres of radius  $a = 82.5$  nm (polydispersity  $< 5\%$ ), with  $a$  determined by small-angle x-ray form factor measurements. Details on the particle synthesis and properties are given in [15]. The spheres have been suspended in distilled water with well-controlled amounts of NaCl added to an initially deionized system. The XPCS experiment was performed at the Troika III of the Troika beam line ID10A at the European Synchrotron Radiation Facility. A schematic view of the setup and experimental details are given in [16]. Measurements were performed at  $\lambda = 1.55$  Å. The coherent beam is provided by a  $12$   $\mu\text{m}$  pinhole placed at  $25$  cm from the sample. With this setup the primary beam intensity was about  $10^9$  photons/s/mA. Photons are detected by a Bicron scintillation counter equipped with an adjustable pair of slits of  $150 \times 150$   $\mu\text{m}^2$ . Correlation functions are calculated in real time via an ALV-5000 digital correlator. Figures 1 and 2 include experimental results of  $S(q)$ ,  $H(q)$ , and of the  $q$ -dependent collective diffusion coefficient  $D(q) = D_0 H(q)/S(q)$ , for two samples of low-salt ( $0.5$  mM NaCl) and high-salt ( $50$  mM NaCl) content, labeled as LS and HS, respectively, (cf. Table I). The ionic strength in the LS sample was chosen such that the system is in the noncrystalline state. Samples LS and HS are within the  $\phi$  range where hydrodynamic screening had been reported to

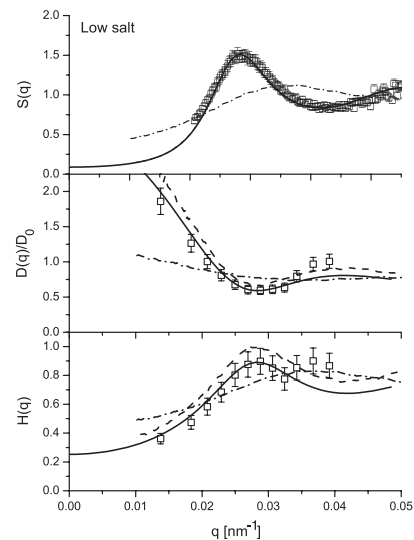


FIG. 1. Static structure factor  $S(q)$ , short-time collective diffusion coefficient  $D(q)$ , and hydrodynamic function  $H(q)$  for a low-salt suspension of charged latex spheres (sample LS:  $0.5$  mM NaCl). Comparison between experiment (open squares),  $\delta\gamma$  theory with RY input for  $S(q)$  (solid lines), and ASD simulation data (dashed lines). Dashed-dotted lines: ASD result for a hard-sphere suspension with same  $\phi$  as in sample LS.

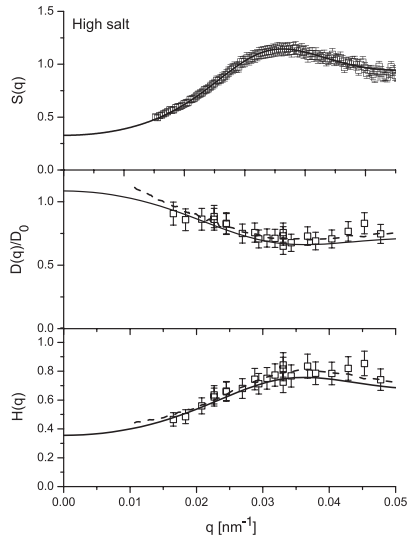


FIG. 2. Same as in Fig. 1 but for a high-salt sample (HS) with 50 mM NaCl.

occur [7]. We have managed to determine  $D(q)$  with great precision from the genuine short-time decay of the XPCS scattering function, in contrast to the work in [7] where  $D(q)$  for the deionized sample was determined from a narrow and noisy part of the intermediate scattering function. As seen in Figs. 1 and 2, the experimental  $S(q)$  of both samples are in excellent accord with Rogers-Young (RY) integral equation calculations [2,17], made using the standard macroion fluid model of charge-stabilized spheres. The effective pair potential in this model is the sum of a hard-core repulsion and the effective pair potential [1],

$$u(r)/k_B T = L_B Z^2 \left( \frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r}, \quad r > 2a, \quad (2)$$

acting between two spheres. The screening parameter  $\kappa$  is determined by colloid surface-released counterions and salt ions. The only adjustable parameter is the effective charge number  $Z$ , which we have selected to match the maximum in  $S(q)$  (cf. Table I for a list of parameters). The RY scheme is very accurate for charge-stabilized suspen-

TABLE I. Parameters used in ASD and  $\delta\gamma$  theory calculations for the low-salt (LS) and high-salt (HS) samples. Charge number  $Z$ : determined from ASD and Rogers-Young  $S(q)$  fits to experimental peak heights. Radius used in calculations:  $a = 82.5$  nm. Temperature:  $T = 293.15$  K. Single-sphere diffusion coefficient:  $D_0 = 2.69 \times 10^{-8}$  cm<sup>2</sup>/s, using a hydrodynamic radius  $a_h = 80$  nm determined from dynamic light scattering. Bjerrum length of water:  $L_B = e^2/(\epsilon k_B T) = 0.71$  nm ( $\epsilon = 80.1$ ). Weight fraction of spheres: 231 g/l. The two slightly different volume fractions have been obtained from matching the peak location of the experimental  $S(q)$ .

|    | $\phi$ | salt (M)           | $Z_{\text{ASD-RY}}$ | $\kappa a$ | $D_s^{\text{ASD}}/D_0$ | $D_s^{\delta\gamma}/D_0$ |
|----|--------|--------------------|---------------------|------------|------------------------|--------------------------|
| LS | 0.123  | $5 \times 10^{-4}$ | 1400                | 6.8        | 0.83                   | 0.735                    |
| HS | 0.142  | $5 \times 10^{-2}$ | 1400                | 85         | 0.73                   | 0.699                    |

sions [2]. Only the RY- $S(q)$  are shown since they are practically coincident with the ASD simulation data in the whole displayed  $q$  range. The RY- $S(q)$  is used as input to the  $\delta\gamma$  calculations. From Figs. 1 and 2, one can see for both samples that the  $\delta\gamma$  theory results for  $H(q)$  and  $D(q)$  compare rather well with the results from the more elaborate ASD simulations. We have verified the validity of a finite system-size scaling procedure [5] also for charged particles, by considering simulation runs with an increasing number  $N = 125$ –860 of spheres. The procedure leads to  $H(q)$  practically independent of  $N$ .

Within experimental uncertainty, both the ASD and  $\delta\gamma$  theory results are in good accord with the experimental data. This good agreement is remarkable, particularly regarding  $D(q)$ , a quantity obtained more directly through experiment than  $H(q)$  from a first cumulant analysis of the dynamic scattering function [1,2]. Whereas the variations in  $q$  of the simulated  $H(q)$  are well captured by the  $\delta\gamma$  scheme, the ASD  $H(q)$  is underestimated overall. This finding can be easily understood: in  $\delta\gamma$  theory applications to charged particles, the self-part of  $H(q)$  is approximated by its value for a hard-sphere suspension at the same  $\phi$ , independent of particle charge and screening parameter [9]. The actual charged-sphere  $S(q)$  enters in  $\delta\gamma$  theory only into the distinct part of  $H(q)$ . This fact allows us to improve the  $\delta\gamma$  scheme by substituting the simulation input for  $D_s$ . Since the charged-sphere  $D_s$  is larger than the hard-sphere value at the same density, this substitution merely shifts the  $\delta\gamma$  prediction of  $H(q)$  upwards, by an amount depending on the parameters under consideration. We find that this hybrid- $\delta\gamma$  scheme is in good accord with all our ASD simulation results for charged suspensions. Figures 1 and 2 do not show the hybrid- $\delta\gamma$  results for  $H(q)$  and  $D(q)$ , since these are nearly coincident with the ASD data. It is evident that the ASD predictions of  $D(q)$ ,  $H(q)$ , and  $S(q)$  for a hard-sphere suspension with the same density as in sample LS, are clearly different from those of sample LS. In particular, the maximum in  $H(q)$  is smaller and located at a larger wave number.

The electrostatic screening in the case of the HS sample is so large ( $\kappa^{-1} < 0.01a$ ), that  $H(q)$  is practically equal to the equal-density hard-sphere form. The maximum,  $H(q_m) = 0.81$ , of the simulated  $H(q)$  at wave-number  $q_m$  is in accord with the linear expression,  $H(q_m) = 1 - 1.35\phi$ , quantifying very accurately the peak height of hard spheres for all  $\phi < 0.5$ . This  $\phi$  dependence for hard spheres has been established through comparison with Lattice-Boltzmann [5,18] and SD simulations [19], dynamic light scattering experiments [18], and numerically exact low density calculations [20]. For comparison, the  $\delta\gamma$  theory prediction for hard spheres with Percus-Yevick input for  $S(q)$ , is well parametrized by  $H(q_m) = 1 - 2.03\phi + 1.94\phi^2$ , with values located moderately below the linear form for all  $\phi < 0.35$ . To summarize and highlight the points discussed above, we compare now the density dependence of  $H(q_m)$  for hard spheres with that of completely deionized charge-stabilized suspensions, and to

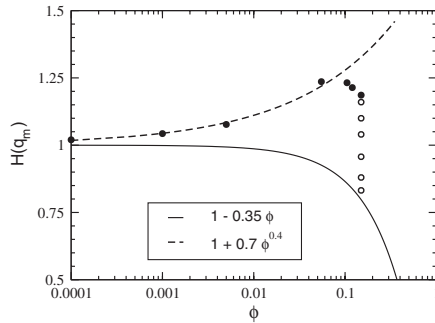


FIG. 3. Maximum of  $H(q)$  vs  $\phi$ . Dashed line:  $\phi$  dependence for deionized dilute suspensions; solid line: hard spheres; filled circles: ASD simulation data for salt-free systems; open circles: ASD data for systems with added 1-1 electrolyte (amount increasing from top to bottom). System parameters: Bjerrum length  $L_B = 5.62$  nm, sphere radius  $a = 100$  nm, and effective charge  $Z = 100$  (assumed fixed).

explore changes in  $H(q_m)$  induced by adding salt. Such a comparison, which is representative for charge-stabilized suspensions, is shown in Fig. 3. The effective charge has been selected to obtain a model system which remains in the liquid state, even when deionized, up to a large volume fraction of  $\phi = 0.15$ . For small  $\phi$ , the  $H(q_m)$  of deionized systems increases for fixed  $Z$  according to  $H(q_m) \approx 1 + 0.7\phi^{0.4}$ . A fractional  $\phi$  dependence with exponent 0.4 was found in earlier work where the full form of the two-body HI had been considered, but without many-body corrections [20]. When  $\phi$  is further increased (beyond  $\phi \approx 0.06$  in Fig. 3), many-body HI becomes important. It causes  $H(q_m)$  to decrease with increasing  $\phi$  due to enlarged hydrodynamic hindrance. When 1-1 electrolyte is added for a fixed  $\phi$  (here:  $\phi = 0.15$ ),  $H(q_m)$  decreases monotonically towards the hard-sphere value (open circles in Fig. 3). The upper most data point with nonzero salt corresponds to  $\kappa a = 1.99$ ; the lowest data point close to the hard-sphere line is the result for the largest amount of salt considered, corresponding to  $\kappa a = 10.15$ . Likewise, the maximum in  $S(q)$  decreases from 2.8 for zero salt (the system is then rather close to the freezing transition) to the hard-sphere-like value 1.15 at  $\kappa a = 10.15$ . The maxima in  $S(q)$  and  $H(q)$  are located practically at the same wave number  $q_m$ . Finally, we point out that according to simulation and  $\delta\gamma$  theory alike, the  $H(q_m)$  with added salt always lies between the zero-salt and hard-sphere curves.

In summary, we have shown that our experimental  $H(q)$  for charged latex spheres are quantitatively describable by the ASD simulation results, also for low-salt suspensions, and even in the range of concentrations where hydrodynamic screening had been reported to occur. The behavior of  $H(q)$  for dense charge-stabilized suspensions, in particular, values of  $H(q_m)$  smaller than 1, is explainable by

many-body HI *without* hydrodynamic screening. Two generic relations between charged-sphere systems (CS) and equal-density hard-sphere systems (HS) are found to be valid, namely  $H^{\text{CS}}(q_m; \phi) > H^{\text{HS}}(q_m; \phi)$  and  $D_s^{\text{CS}}(\phi) > D_s^{\text{HS}}(\phi)$ . Even without an improved input for the self-part of  $H(q)$ , the  $\delta\gamma$  theory is found to be useful for predicting, on a semiquantitative level, general trends in the behavior of  $H(q)$  and  $D(q)$  for charge-stabilized suspensions.

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