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# Electrophoretic mobility of electrostatically interacting colloidal spheres

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## Abstract

We have measured the electrophoretic mobility  $\mu = v_E/E$  (where  $E$  is the electric field strength and  $v_E$  the electrophoretic velocity) of highly charged colloidal spheres in deionized aqueous suspension at particle number densities  $n$  between 0.15 and 150  $\mu\text{m}^{-3}$ . Under these conditions the system exhibits fluid or crystalline order. We used laser Doppler velocimetry to determine the electrophoretic velocities  $v_E$  as spatially averaged particle velocities from both integral and spatially resolved measurements. With this approach we were for the first time able to extend measurements far into the crystalline region of the phase diagram. We found  $\mu$  to be constant at low  $n$  while at large  $n$  we observe an approximately logarithmic decrease in  $n$ . However, the descent of  $\mu$  is not affected by the phase transition. This indicates that this transport coefficient rather depends on the local structure of the ionic clouds surrounding the particles than on the long range order of the suspension.

## 1. Introduction

The equilibrium properties of model colloidal suspensions are believed to be well understood. These consist of submicron solid particles of equal size and usually spherical shape dispersed in a carrier fluid. Like for atomic matter one observes colloidal fluids, crystals and glasses [1–4]. Recently the focus shifted to more complicated situations such as phase transition kinetics or the behaviour of mixtures [5–7]. The fundamental understanding of their behaviour in external fields, however, remains a challenge to theory, simulation and experiment [8]. A benchmark test for the theoretical treatment of transport processes in statistical mechanics in general and for the electrokinetic theories in particular is given by the particle concentration dependence of the electrophoretic mobility  $\mu = v_E/E$  of model colloids [9]. Here  $v_E$  denotes the stationary electrophoretic drift velocity of particles subjected to a homogeneous electric field  $E$ . Thus far, experiments at elevated salt concentrations have dominated the literature where, in general, standard theories for non-interacting particles were confirmed. Only few experiments under low salt or deionized conditions were reported [10–13], however, with some

surprising results. For example, Evers *et al* [14] reported an increase of  $\mu$  with increasing particle concentration for deionized suspensions in a disordered state and a saturation of  $\mu$ , once short range order was established and once the counter-ions released by the particles start dominating the small ion concentration, respectively. These experiments performed on large particles of 300 nm diameter were not extended to the crystalline phase because of the high sample turbidity. In a subsequent experiment on smaller particles we have been able to extend the measurements far into the crystalline region [15]. However, there the evaluation was significantly complicated by a complex flow behaviour of the sample. We base our evaluation here on additional measurements of the complete flow profile  $v(x, y)$  and for the first time are able to report on the systematic  $n$ -dependence of  $\mu$  in the crystalline state.

## 2. Experimental details

We used poly- $n$ -butylacrylamide-polystyrene co-polymer particles which were a kind gift of BASF AG Ludwigshafen, lab code PnBAPS68. Particles were synthesized in a surfactant free emulsion polymerization and are stabilized by sulfate surface groups stemming from the initiator. PnBAPS68 has been thoroughly characterized before by various methods [16]. The particle diameter (ultra-centrifugation) was  $2a = d_{50} = 68$  nm with a polydispersity index of  $\sigma = 0.02$ . The titrated surface group number was  $N = 1.4 \times 10^3$ . Effective charges from conductivity and elasticity were  $Z_{\sigma}^* = 450$  and  $Z_G^* = 327$ , respectively. As discussed in detail in [16], both were found to be independent of particle concentration.

Samples with different particle number density  $n$  were prepared from pre-cleaned stock suspensions by dilution with doubly distilled water. As in our previous experiments all sample conditioning took place in a closed, gas-tight tubing system under inert gas atmosphere [17]. The system connects several devices including a reservoir for adding water or suspension, an ion exchange column, a conductivity experiment and several optical cells for performing laser Doppler velocimetry (LDV), static light scattering and video microscopy. The particle number density  $n$  was inferred from a combined Bragg scattering and conductivity experiment on the deionized sample [18]. During preparation the suspension is driven through the circuit by a peristaltic pump. Completion of deionization is monitored via the time dependence of the conductivity. Typical residual ionic impurity concentrations are of the order of the ion product of water. For  $n > n_F$ , the freezing density, the sample is kept in a shear molten state but readily crystallizes once shear is aborted. Further details of the preparation have been given elsewhere [15–17]. The electrophoretic cell was of rectangular cross section with depth  $\times$  height =  $d \times h = 1 \times 10$  mm<sup>2</sup>. The origin of our coordinate system is at the cell centre with  $x \parallel d$ ,  $y \parallel h$  and  $z \parallel v_E$ . During the measurements the electrode chambers are sealed against the remaining preparation circuit by electromagnetic valves, closed upon cessation of pumping. Alternating square wavefields of up to  $E = |\pm 80|$  V cm<sup>-1</sup> were applied at switching frequencies  $f_{AC} = 0.05$ – $0.2$  Hz. Measurement intervals were restricted to one field direction, starting 2 s after field reversal and ending 1 s before the next field reversal to obtain quasi-DC conditions. In the presence of an electric field an electro-osmotically driven parabolic solvent flow develops. As  $v_E = \text{constant}$  the particle flow profile is also parabolic:  $v_P(x, y) = v_E + v_S(x, y)$ . Furthermore, due to the solvent's incompressibility, the spatially averaged solvent velocity  $\langle\langle v_S(x, y) \rangle\rangle_x = 0$ . Vice versa, the electrophoretic velocity equals the  $x$ - and  $y$ -averaged particle velocity  $v_E = \langle\langle v_P(x, y) \rangle\rangle_x = \langle\langle v_P(x, y) \rangle\rangle_y$ . For non-interacting systems with strictly parabolic flow profile it has been shown that a simple  $x$ -average at known cell height  $y$ ,  $\langle v_P \rangle_x(y)$ , is sufficient for deriving the electrophoretic velocity  $v_E$  [19]. It was checked that this applies also for fluid order, while for crystalline order the full average had to be taken.

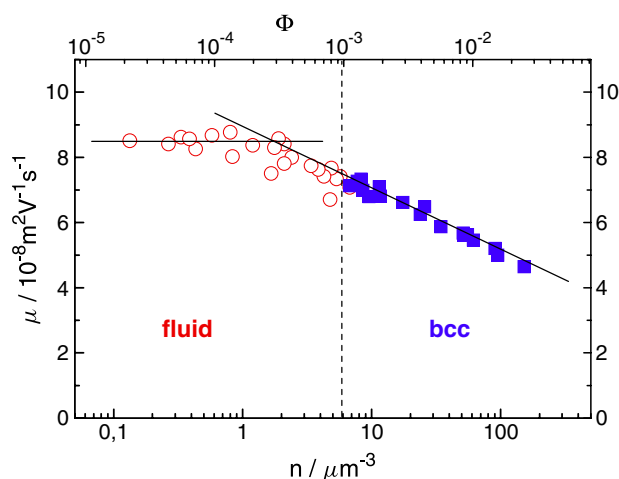
Particle velocities were obtained from LDV using an integral or spatially resolved superheterodyne reference beam measurement [15, 19]. The illuminating and reference beam were crossed at mid-cell height under an angle of  $\Theta = 18.87^\circ$ . The Doppler shifted light scattered off each illuminated particle is superimposed on the distant detector with a reference beam having an independently fixed frequency shift of 2 kHz. In this technique the homodyne (self-beating) terms and low frequency noise remain at zero frequency and are well separated from the superheterodyne part which is further evaluated. The latter yields the distribution of velocities in a given scattering volume as a power spectrum centred about the reference frequency of 2 kHz. Using suitable detection optics, we alternatively observed the full depth of the cell (integral measurement) or obtained the flow profile from a series of restricted  $x$ -range measurements with  $70 \mu\text{m}$  resolution in the  $x$ -direction. We carefully checked that the two approaches yielded identical  $x$ -averaged velocities  $\langle v_p \rangle_x(y)$  for a given measurement height  $y$ , field strength and particle concentration. Thus in the fluid state, parabolic flow profiles apply and, like in the disordered state, the electrophoretic velocity  $v_E$  can be calculated directly from  $\langle v_p \rangle_x(y)$  [19]. In the crystalline state, flow profiles are non-parabolic. We therefore repeated the measurements also at different heights  $y$  of the cell to obtain the full flow profiles and allow us to infer the electrophoretic velocity as the  $y$ -average of  $x$ -averaged particle velocities  $v_E = \langle \langle v_p(x, y) \rangle_x \rangle_y$ . These spatially resolved measurements in combination with microscopic observations further yielded valuable information on the complex multiphase flow behaviour under the combined action of electrophoresis and electro-osmotic solvent flow. For a detailed description and examples of spectra the reader is referred to [15]. The electrophoretic mobility is then again calculated as  $\mu = v_E/E$ .

### 3. Results and discussion

Results for the measured particle concentration dependence under deionized conditions are presented in figure 1.  $\mu$  stays practically constant at  $\mu \approx 8.5 \times 10^{-8} \text{ m}^{-2} \text{ V}^{-1} \text{ s}^{-1}$  for about one order of magnitude in  $n$ . It then descends in an approximately logarithmic fashion. Note the occurrence of a phase transition from fluid to body centred cubic (bcc) structure with a narrow coexistence region located at  $n = 6.1 \pm 0.5 \mu\text{m}^{-3}$  and  $\Phi \approx 10^{-3}$ . This transition does not affect the descent of  $\mu$  with  $n$ .

A few comments are in order. First, in the fluid state the mobility is large. This is consistent with the observations of Deggelmann *et al* who studied spheres with decreasing salt concentration [11]. As soon as the fluid state was entered, the mobility rose to large values of the same order as those observed here. This is seemingly at variance with the observations of Okubo [10] and Garbow [13], who studied isolated spheres with decreasing salt concentration to obtain rather low mobilities of the order of  $\mu \approx 3 \times 10^{-8}$  and  $0.8 \times 10^{-8} \text{ m}^{-2} \text{ V}^{-1} \text{ s}^{-1}$  (in a water/glycerol mixture), respectively. There, however, no fluid order had developed. Both data sets are bridged by the study of Evers *et al* [14] who investigated the increase of mobility from low to large values of  $n$  in the deionized state. For the fluid state these authors reported a plateau, much like that observed in the present study. The origin of this plateau, however, is still unclear.

Second, a decrease of mobilities with increased particle concentration was observed before for rod-like TMV-virus particles in the deionized state [12]. There it was attributed to a change of the state of dissociation of carboxyl virus surface groups. As in our case particles are stabilized by strong sulfate surface groups, we do not consider this possibility here. We rather presume that the observed decrease can be well explained within usual electrokinetic models. These consider the dependence of  $\mu$  on  $\kappa a$ , where  $\kappa$  is the Debye screening parameter and  $a$



**Figure 1.** The reduced electrophoretic mobility versus the decadic logarithm of the particle number density  $n$  (lower scale) and packing fraction  $\Phi$  (upper scale) for PnBAPS68 under fully deionized conditions. Open symbols: fluid state; closed symbols: crystalline state. The vertical dashed line gives the equilibrium fluid–bcc phase transition (note that the coexistence region is too small to be resolved on this scale). The mobility first stays constant with increasing particle concentration, then decreases in an approximately logarithmic fashion. Solid lines are guides to the eye.

(This figure is in colour only in the electronic version)

the particle radius. Here  $\kappa a$  will increase at constant deionized conditions with the square root of  $n$  due to the contribution of the particle counter-ions. For  $\kappa a$  increasing from 0.1 to 1 and a constant surface or  $\zeta$ -potential of 175 mV, standard theories predict a decrease of  $\mu$  from about  $7 \times 10^{-8}$  to  $5.5 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  [9]. Alternatively, as suggested from conductivity or shear modulus measurements, we may assume a constant effective charge of e.g.  $Z_{\mu}^* = 400$  to find the surface potential to decrease from 200 mV to some 120 mV for the same range of  $\kappa a$ . Estimates of the resulting  $\mu$  show a slightly steeper decrease with  $\kappa a$ . Both assumptions are thus compatible with our data. A quantitative evaluation including approaches based on numerically calculated effective charges [20] is under way.

Finally, we note that the mobility is not affected by the phase transition to the crystalline state occurring at about  $6 \mu\text{m}^{-3}$ . In particular we have performed measurements close to the phase transition, where the suspension is originally in the crystalline state but is shear melted in the course of time. Also there we found  $\mu$  to be independent of the suspension structure. The local velocity  $v_p$ , on the other hand, is strongly affected by the development of long range order and the corresponding shear rigidity. This leads to the observed non-parabolic flow profiles and prevents a direct evaluation of local  $v_p(x, y)$  or  $\langle v_p \rangle_x(y)$  for  $v_E$ . The spatially resolved measurements performed and the evaluation procedure employed then allowed us to average out the local flow properties. Previous studies had reported only few data points for crystal mobilities similar to those of the fluid state [11, 14]. In both cases statistical arguments did not allow further conjectures. From conductance measurements, however, it is known that the conductivity is also not influenced by this phase transition [21]. This seemingly general insensitivity of electrokinetic properties to the suspension structure indicates that the electrophoretic mobility (and also conductivity) is in a sense an individual particle effect. As for isolated or non-interacting particles,  $\mu$  only depends on the geometry and surface potential of a given particle species. We stress, however, that since the potential itself depends on the

presence of neighbouring particles, our measurements actually imply that the potential does not change notably across the transition.

#### 4. Conclusion

We have sketched a scheme for measuring the electrophoretic mobility of charged particles in strongly interacting suspensions, where the finite shear rigidity of the crystalline state leads to ill defined, non-parabolic flow profiles. This averaging procedure should be applicable to a large variety of systems showing multiphase flow. Further, the present study has shown that the general electrophoretic behaviour of spherical colloids at large particle concentration shows first a plateau and then a decrease with increasing  $n$ . This is qualitatively consistent with previous work on the low concentration side showing an increase ending in a plateau. We finally showed that  $\mu$  was not affected by the phase transition from fluid to crystalline order. This could be rationalized by considering that it actually denotes a constancy of the surface potential across the transition and, in contrast to  $v_P$ , is independent of the local crystal cohesion.

We believe that our data provide a challenging data base for the theoretical modelling of electrophoretic transport at low salt conditions. Some attempts to understand electrophoretic transport under conditions of strong electrostatic interactions have already been made by several theoretical groups invoking the charge renormalization concept or other similar approaches [22, 23]. One open question is the dependence of the surface potential on the suspension conditions; another relates to the connection between a given surface potential and observable  $\mu$ . While the origin of  $\mu$  from microscopic counter-ion flow along a charged surface is well established [9], its modification under the presence of neighbouring particles remains to be clarified. It is fair to say that we are still far from a comprehensive theoretical understanding of the issue. We hope to have presented novel and stimulating data supporting further theoretical advance in this area.

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