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Charged colloidal suspensions and their link to complex plasmas

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Abstract. Charged colloidal dispersions and complex plasmas share the classical many-body character of strongly coupled systems but differ in their dynamics, which is overdamped in the colloidal and almost ballistic in the complex plasma case. In this paper, we shall discuss basic properties of charged colloids and emphasize in particular their link to complex plasmas. Similarities and differences between colloids and complex plasmas are discussed. In particular, the charging process in colloidal suspensions, their interactions and the Brownian dynamics is outlined.

Keywords: charged colloids, complex plasmas, interactions, dynamics

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I. Introduction

There is a strong interdisciplinary link between charged colloidal dispersions and complex plasmas. Charged colloids comprise mesoscopic particles which are typically highly charged and are embedded in a liquid solvent. This makes them similar and also different to complex plasmas: the latter are also highly charged but are embedded in a plasma. Static equilibrium properties only depend on the interaction forces, which are screened Coulomb forces in both systems. This results in similar behaviour for the structural correlations and equilibrium phase transitions. The particle dynamics, however, is different. It is strongly overdamped and also complicated by solvent-mediated hydrodynamic interactions for the colloidal particles, while the dynamics is ballistic (virtually undamped) for dusty plasmas.

In this paper, we summarize some basic properties of charged suspensions and put them into context in the world of complex plasmas. First of all, basic facts of the charging process in colloids are discussed and the effective Yukawa-like interaction is introduced. Then, we discuss briefly the dynamics and highlight the differences between dusty plasmas and colloids. In particular we then introduce hydrodynamic interactions which are non-Hamiltonian and therefore possess an analogy to the wake-induced interactions in dusty plasmas.

II. Charging of colloids

Immersion of colloidal particles in a liquid medium *always* leads to some degree of charging. Entropy leads to dissociation of surface groups, or alternatively, absorption of charged species can occur, see Figure 1. While the degree of charging is strongly associated with the medium in which the colloids are dispersed, we stress that true neutral hard spheres do not exist. However, the degree of charging is often so small that it can reasonably be neglected [1].

The most common medium in which colloids are dispersed is water. Now one can gain a qualitative understanding of what sort of charging might be expected simply by applying Coulomb's law, noting the typical ion size (a few Angstroms) and the dielectric constant of the solvent. This leads to an ion-site binding energy of a few times the thermal energy $k_B T$ in the case of water and monovalent ions, in which case we expect that entropy leads to a large degree of dissociation and strong charging.

At a given added salt concentration which contains both counter- and coions, the colloidal charging process quickly approaches dissociation-association equilibrium of the counterions. Strictly speaking the resulting colloidal charge number Z is fluctuating (as it is for the dusty plasma case) but typically these charge fluctuations are ignored and a fixed charge is assumed. It is, however, essential that the sign and the actual charge number depends on the thermodynamic parameters such as salt concentration, colloid density and system temperature as well as on the material properties of the colloidal surface and the solvent. The process of charge adjustment to the actual environment is called *charge regulation* [2]. In principle instead of dissociation of charged groups, the inverse process of adsorption of charged species can occur as well.

This interaction between a colloid and its counterion has potentially profound consequences for the thermodynamics of the system. In particular, it has been suggested that ion-colloid coupling could, under some circumstances, lead to phase separation into a colloid-rich and colloid-poor phases [3]. This is interesting as the direct colloid-colloid interactions are repulsive at the two-body level[4] which would be expected to suppress phase separation, which has nonetheless been observed experimentally [5].

For the same colloid material one expects roughly a scaling of the bare colloidal charge with the area, i.e. $\propto \sigma^2$ with σ denoting the particle diameter. This scaling simply relies on the idea that the surface charge density is the same, but to our knowledge has never been tested directly in experiments. Typical charge numbers obtained for micron-size colloidal particles are around $Z=10-100,000$ elementary charges, therefore the colloidal particles are called *macroions* (or polyions). This of course implies that dissociated ionic groups are attracted back by the oppositely charged colloidal surfaces. One therefore splits the charge (a bit arbitrarily) into a so-called Stern layer very close (within a nanometer) to the colloidal surfaces. This Stern layer contains mobile charged groups which are still strongly attracted by the colloidal surfaces and mobile charges which are in the solution [2]. It is typical for the mobile ions that a screening theory is applied leading in simplest linearized form to a screened Coulomb (Yukawa) orbital of charge density around the colloidal charge.

One actual problem of colloid charging is that the bare colloid charge Z cannot be measured directly. One possible approach is a titration experiment. The *titration charge*,

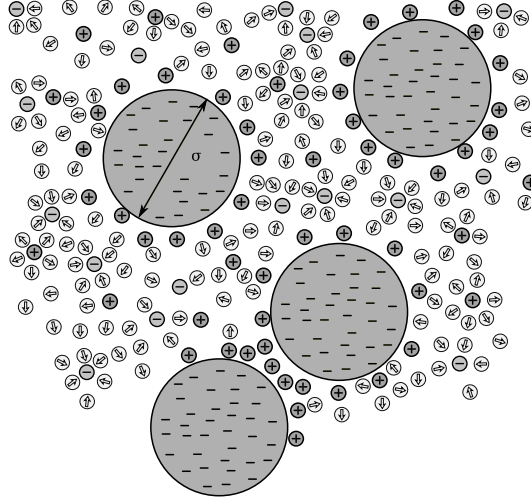


FIGURE 1. A charged colloidal suspension consists of macroions (large grey spheres) with a mesoscopic diameter σ and a charge Z of 100-100,000 elementary charges, microscopic counterions (dark and bright small grey spheres) which are typically monovalent or divalent and the molecular polar solvent (white) shown as small particles (the arrows denoting the electric dipole moments). Two macroions repell themselves due to the Coulomb repulsion of an overlapping electric double layer.

however, only gives an upper bound to the colloid charge number Z as all ionizable groups on the colloidal surface are probed. This clearly does not imply that all of these groups are dissociated under actual experimental conditions. Another option to access the colloidal charge experimentally is an electrophoretic experiment where an external electric field is applied and the resulting drift motion of the colloid is measured. This gives the so-called *electrophoretic charge*. Nevertheless, since the counterions are moving with the electric field the measured electrophoretic charge is in general not identical with the bare charge Z .

III. Pair interaction between charged colloids

If one assumes *a priori* linear Poisson-Boltzmann theory, then the celebrated Derjaguin-Landau-Verwey-Overbeek [6] pair interaction $V(r)$ between colloids reads

$$\beta V(r) = \begin{cases} \infty & \text{for } r < \sigma \\ \beta \epsilon \frac{\exp(-\kappa(r - \sigma))}{r/\sigma} & \text{for } r \geq \sigma \end{cases} \quad (1)$$

where r is the centre to centre separation of the two colloids. The contact potential is given by

$$\beta \epsilon = \frac{Z^2}{(1 + \kappa \sigma/2)^2} \frac{\lambda_B}{\sigma} \quad (2)$$

where $\beta = 1/k_B T$, Z is the colloid charge, σ is the colloid diameter, the inverse Debye screening length $\kappa = \sqrt{4\pi\lambda_B\rho_{ion}}$ where ρ_{ion} is the density of small ions. Here, the Bjerrum length is $\lambda_B = e^2/(k_B T \epsilon_r \epsilon_0) = 0.7\text{nm}$ in the case of water. Note that the DLVO interaction takes a Yukawa or screened Coulomb form. In fact, when the charging increases, or, more specifically, the electrostatic potential increases, linear Poisson-Boltzmann theory breaks down. In water this typically occurs with colloids exceeding a few hundred nanometers in diameter. However, developments in surface chemistry treatments allow a considerable degree of control over the charging [7].

Even at these elevated degrees of charging, Alexander *et. al.* [8] showed that except for small distances (where van der Waals interactions would come into play) the interaction is still of a Yukawa form, but with a smaller, *renormalised* charge. This implies that the effective interaction charge is getting renormalised towards much smaller values at high Coulomb coupling, a concept called *charge renormalization*. Typically, far away from the colloidal centres linearized screening theory holds with an asymptotic charge such that simple estimates of the effective saturated charges Z_{eff}^{sat} are possible [9, 10].

$$Z_{eff}^{sat} = 2\sigma(1 + \kappa\sigma/2)/\lambda_B \quad (3)$$

This is the effective charge one would attribute to a single particle in a salty environment if the bare charge is (formally) increased towards infinity. According to Eqn. 3, there are two different regimes: if $\kappa\sigma \ll 1$ is small, as typical for dusty plasmas but also realized for strongly deionized colloids or systems with apolar (low dielectric constant) solvents, the main scaling of Eqn.3 is linear in the particle diameter σ , similar as for a complex plasma. For strong screening, on the other hand, as typical for highly salted suspensions, there is a quadratic scaling with the particle diameter σ .

With a fitted effective charge, most of the experimental behaviour can indeed be conveniently interpreted with the linearized Poisson-Boltzmann theory such that the DLVO approach is a cornerstone to describe charged colloids [11, 12, 4]. As very many studies have shown, for example Monovoukis and Gast [13, 14], the DLVO theory with charge renormalisation is among the most successful approaches to describing charged colloids. Triplet interactions can be shown to be small [15].

IV. Dynamics of colloids and dusty plasmas

The equation of motion for a particle i at position $\vec{r}_i(t)$ (t denoting time) is in general given by

$$m_i\ddot{\vec{r}}_i + \gamma\dot{\vec{r}}_i = \vec{F}_i(\{\vec{r}_n(t)\}) + \vec{f}_i(t) \quad (4)$$

where m_i is the particle mass, γ its damping constant and \vec{F}_i the total force acting on particle i from an external field or the interaction with neighbouring particles. The random force \vec{f}_i is Gaussian distributed with zero mean variance

$$\overline{f_i^{(n)}(t)f_j^{(m)}(t')} = 2\gamma k_B T \delta_{ij}\delta_{nm}\delta(t-t') \quad (5)$$

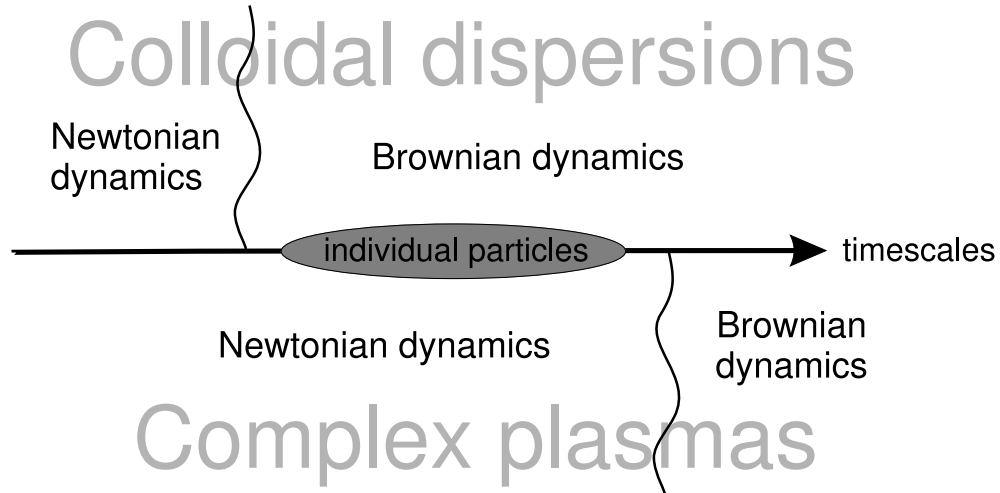


FIGURE 2. Schematics of dynamical regimes in complex plasmas and colloidal dispersions. The individual particle dynamics is fully damped in colloidal dispersions and virtually undamped in (strongly coupled) complex plasmas. The hydrodynamic timescales for both media are in the Brownian dynamics regime.

Here, (n) and (m) denote the different Cartesian components and the overbar is a noise average.

In colloidal dispersions, the inertia term $m_i \ddot{\vec{r}}_i$ in Eqn. 4 is negligibly small due to the time scale separation between the microscopic solvent kicks and the macroscopic damped motion of particles. Therefore, we end up, for colloids, with completely overdamped motion. The time domain where Newtonian dynamics holds is extremely small, see Figure 2. For complex plasmas, on the other hand, the damping $\gamma \dot{\vec{r}}_i$ is small compared to the inertia term, leading to an almost undamped deterministic motion. Recall that the stochastic forces vanish in the undamped case. Therefore, the crossover from Newtonian to Brownian dynamics is shifted to much larger time scales, see again Figure 2.

Figure 3 shows two snapshots for an interacting many particle system. The interaction potential is Yukawa-like in two dimensions. In Figure 3a, the equations of motion with $\gamma = 0$ are shown (close to the virtually undamped dusty plasma case), while in Figure 3b the stochastic equations of motion with $m_i = 0$ (colloids) are shown for a typical representation of the random forces. The corresponding particle trajectories $\vec{r}_i(t)$ are completely different in both cases. This leads to different behaviour in dynamical correlation functions.

V. Hydrodynamic interactions

Hydrodynamic interactions describe forces which are mediated between colloidal particles via a solvent flow. If a colloidal particle is moving relative to the embedding fluid according to a force, it creates a fluid velocity field around it which then affects the motion of neighbouring colloidal particles, see Figure 4. Typically, the colloidal velocities are so small that the fluid motion is in the low Reynolds number regime, and

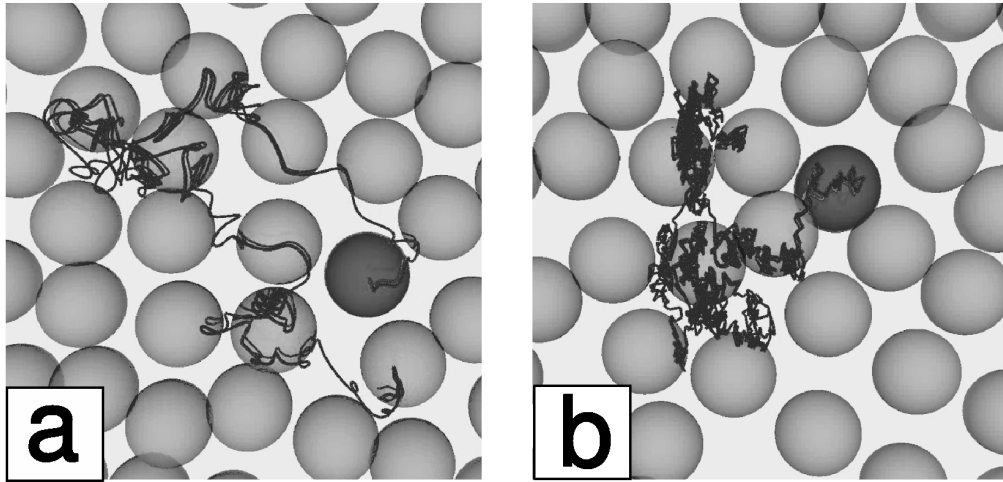


FIGURE 3. Typical particle trajectories for a) Newtonian dynamics b) Brownian dynamics. The interaction and starting configuration (as given by the neighbouring grey spheres) are the same.

a linearized relation between exerted force and the resulting colloid drift velocity for the neighbouring particles can be assumed. As a leading order approximation at the pair level, hydrodynamic interactions in the far field give a $1/r$ - coupling. This forms the basis for the Rotne-Prager tensor described below.

It is important to note that there is a fundamental difference between hydrodynamic interactions and direct interactions. The latter affect the static equilibrium properties (such as structural correlations and equilibrium phase transitions), while the former have no impact at all on static equilibrium statistics. In equilibrium, in fact, all static properties can be derived from the Boltzmann distribution which is independent of hydrodynamic interactions. However, dynamical correlations in equilibrium and nonequilibrium phase transition can be influenced by hydrodynamic interactions. As examples where hydrodynamic interaction do play a major role, we mention the long-time self-diffusion coefficient, the sedimentation speed and behaviour of colloids under shear and other driving fields. In this respect, colloidal hydrodynamic interactions are similar to wake-interactions in complex plasmas: they are non-reciprocal i.e. Newton's third law is violated [16].

A quantitative description of hydrodynamic interactions starts from a general linearized relation between particle drift velocities and forces [17, 18, 19]. In most general form, let us consider N **interacting** particles. Using a compact notation for the particle positions

$$\{x_i\} = \{\vec{r}_i\} = \underbrace{\{x_1, x_2, x_3\}}_{\vec{r}_1}, \underbrace{\{x_4, x_5, x_6, \dots\}}_{\vec{r}_2}, \dots, \underbrace{\{x_{3N-2}, x_{3N-1}, x_{3N}\}}_{\vec{r}_N} \quad (6)$$

we assume a linear relation between acting forces F_n on the particles and the resulting drift velocities v_n using same compact notation for other multiple vectors. The linear

relation is in general

$$v_i = \sum_{j=1}^{3N} L_{ij}(\{x_n\}) F_j \quad (7)$$

where $F_j = -\frac{\partial}{\partial x_j} U_{\text{tot}}$ where U_{tot} involves the total potential energy. The underlying assumption in (7) is that the hydrodynamic interactions act quasi-instantaneously. This is justified by the fact that the timescale upon which a shear perturbation is travelling through the suspension within an interparticle distance is much smaller than that of Brownian motion. The coefficients L_{ij} constitute the so called $3N \times 3N$ mobility matrix and can in principle be obtained by solving the Stokes equations of N spheres with appropriate stick boundary conditions of the solvent flow field on the particle's surfaces.

Now we consider the explicit form for $L_{nm}(\{x_j\})$. The linear relationship (7) can be rewritten as

$$\vec{v}_n = \sum_{m=1}^N \bar{\bar{H}}_{nm} \vec{F}_m \quad (8)$$

where each quantity $\bar{\bar{H}}_{nm}$ is a 3×3 matrix. Solving the linearized Navier-Stokes equations with the appropriate stick boundary conditions on the particle surfaces is a difficult problem. In general, hydrodynamic interactions have **many-body character**, a pair expansion is only possible at low concentrations. Furthermore, hydrodynamic interactions have quite different near-field behaviour for almost touching particles since there are divergent lubrication terms.

In a systematic calculation one just considers a particle pair and performs a multipole-like expansion for large distances between the sphere centers. This leads to the **Rotne-Prager-tensor**

$$H_{nm} = \frac{1}{\gamma}, \quad H_{nm} = \bar{\bar{H}}_{RP}(\vec{r}_n - \vec{r}_m) \quad (9)$$

with

$$\bar{\bar{H}}_{RP}(\vec{r}) = \frac{1}{\gamma} \left(\frac{3 R_H}{4 r} [\mathbb{1} + \hat{r} \otimes \hat{r}] + \frac{1 R_H 3}{2 r^3} [1 - 3 \hat{r} \otimes \hat{r}] \right), \quad \hat{r} = \frac{\vec{r}}{r} \quad (10)$$

where R_H is the hydrodynamic radius of the colloid. This is the leading far field term for two particles at a large distance \vec{r} . The symbol \otimes denotes the dyadic product or tensor product. Higher order expansions of higher order than $\frac{1}{r^3}$ are possible. These also include terms of sphere rotation. From the Rotne-Prager expression it becomes obvious that $L_{nm}(\{x_j\})$ is long-ranged in terms of distances between particles.

For interacting particles, the Langevin equations [17] are given by:

$$\dot{x}_n(t) = \sum_{m=1}^{3N} L_{nm} \left(-\frac{\partial U_{\text{tot}}}{\partial x_m} + f_m(t) \right) + k_B T \sum_{m=1}^{3N} \frac{\partial L_{nm}}{\partial x_m} \quad (11)$$

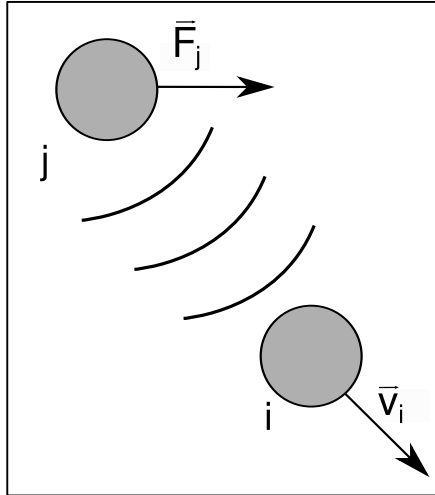


FIGURE 4. Schematic representation of the hydrodynamic interaction: particle j is feeling a force \vec{F}_j which creates a flow field that affects the mean velocity \vec{v}_i of particle i .

with Gaussian random variables f_m which fulfill

$$\overline{\vec{f}_m(t)} = 0 \quad (12)$$

$$\overline{f_m(t)f_{m'}(t')} = 2L_{mm'}^{-1}k_B T \delta(t-t') \quad (13)$$

These equations obviously generalize the equations of motion (4). It is only when hydrodynamic interactions (formally) vanish, i.e. $H_{nm} = \frac{1}{\gamma} \delta_{nm}$ that the equations are the same.

In conclusion, solvent mediated hydrodynamic interactions act instantaneously on the colloidal diffusive time scale and have in general many-body character. It is only for dilute suspensions that they can be decomposed into pairwise tensors. Modern techniques have been designed to simulate hydrodynamic interactions efficiently for various geometric constraints which are e.g. based on lattice-Boltzmann [20] or multiparticle-collision dynamics [21] techniques.

VI. Conclusions

In conclusion, charged colloidal dispersions and complex plasmas share the feature of a classical strongly coupled Coulomb system. Both systems can be approximately described by a Yukawa pair interaction such that equilibrium properties like bulk phase behaviour (fluid-crystal coexistence, etc) are identical. Dynamical processes and nonequilibrium phenomena are different since the particle dynamics is completely overdamped [22] for colloidal dispersions and virtually undamped for dusty plasmas. Therefore, although nonequilibrium phenomena like lane formation [23, 24, 25] and phase separation [26] are qualitatively similar, the dynamical details are different. The dynamics of

all phase transformations which involve a latent heat, for example, are expected to be different: while the latent heat is immediately taken up by the solvent for colloids, it is released mainly to the dust particles in the complex plasma case. These fascinating differences between colloidal [27] and complex plasma [28] crystallization still need further exploration in the future.

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