

# A Statistical Mechanics Approach to Colloidal Suspensions

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## Abstract

Despite the large differences in mass, length and time scales, suspensions of spherical colloidal particles in a solvent share many features of simple atomic liquids, including structure, phase behaviour and even the transition to a glassy state at high concentrations. The analogies, but also the differences, will be illustrated by a few recent applications of the Statistical Mechanics formalism of simple liquids to sterically or charge-stabilized, concentrated colloidal suspensions. Examples include sedimentation equilibrium and non-linear screening of charged colloids by counterions.

## 1. Introduction

A colloidal suspension consists of “mesoscopic” particles in the size range  $10 \lesssim \sigma \lesssim 10^3$  nm, if  $\sigma$  denotes a characteristic diameter, that are dispersed in a suspending fluid. We shall henceforth consider rigid, spherical monodisperse colloidal particles. The main objective of this paper will be to illustrate that, despite the large differences in mass, length and time scales, colloidal suspensions share many features of simple atomic liquids. In a Statistical Mechanics approach to colloidal suspensions, one starts from an *ab initio* basis involving the interparticle forces. For an interparticle distance  $r > \sigma$ , there is an attractive contribution from the van der Waals interaction. In order to prevent irreversible flocculation, a stabilization mechanism is needed. There are essentially two different methods: (a) steric stabilization and (b) charge stabilization. As regards steric stabilization, the colloidal particles are coated with polymer brushes and this leads to an “entropic” repulsion that can, to a good approximation, be modelled by a simple hard-sphere (HS) interaction:

$$V(r) = \begin{cases} \infty & \text{for } r \leq \sigma \\ 0 & \text{for } r > \sigma \end{cases} \quad (1)$$

Charge stabilization results when radicals at the colloidal surface ionize in a polar suspending fluid, forming highly charged macroions (carrying typically 100–1000 elementary charges) and a counterion field. For low macroion densities, linearized Poisson–Boltzmann theory [1] leads to an effective screened Coulomb interaction between macroions which is the electrostatic part of the celebrated DLVO potential

$$V(r) = Z^{*2} \exp(-\kappa r)/\epsilon r \quad (2)$$

where  $\kappa^2 = 4\pi\rho_c q^2/\epsilon k_B T$  is the inverse Debye–Hückel screening length and  $Z^* = Z \exp(\kappa\sigma/2)/(1 + \kappa\sigma/2)$ . Here,  $q$ ,  $\rho_c$  denote the counterion charge and number density and  $Z$

is the bare macroion charge. Moreover,  $\epsilon$  is the dielectric constant of the solvent and  $T$  is the temperature (typically room temperature). Often, the van der Waals interaction is practically suppressed by “index-matching” leaving the two simple pairwise potential models (1) and (2) for investigating the structure of sterically resp. charge stabilized colloidal suspensions. Since simple atomic liquids [2] are described by similar pair potentials, it becomes immediately clear that there must exist direct analogies with atomic systems: in particular, the pair structure is similar; however, it varies on a length scale such that diffraction experiments of visible light rather than X-rays are necessary. Furthermore, the phase diagram is similar; there are, in general, gas, liquid, crystal and glassy phases for colloidal suspensions. In particular, computer simulation studies [3] have revealed that the HS system exhibits a liquid phase up to a packing fraction  $\eta \equiv \pi\rho\sigma^3/6 = 0.49$  (where  $\rho$  is the number density) and then shows a first order phase transition to a (fcc or hcp) solid with  $\eta = 0.54$ . These theoretical values are in good agreement with recent observations on sterically stabilized colloidal particles [4] where also a glassy state beyond  $\eta = 0.60$  was found. For the Yukawa system (2), on the other hand, a bcc to fcc transition occurs in the solid for increasing  $\kappa$  [5].

However, there are also important differences compared to atomic systems. The dynamics are Brownian instead of Newtonian and this has a direct influence on the time-dependent correlations. For example, the scenario of the kinetic glass transition may be different [6]. An advantage is the possibility of “tuning” the interactions (e.g. by adding salt into a charge-stabilized suspension), whereas a disadvantage is the intrinsic polydispersity in size and charge [7–9]. Furthermore, for high macroion concentrations, the pair potential assumption (2) must break down and there are counterion-induced effective many-body-forces between macroions.

In order to illustrate applications of the Statistical Mechanics formulation of simple liquids to colloidal suspensions, we select two recent topics. In Section 2, we discuss sedimentation equilibrium for the HS and Yukawa systems. Secondly, in Section 3, an *ab initio* description of nonlinear counterion screening in charge-stabilized colloidal suspensions is proposed that naturally incorporates effective many-body interactions between the macroions.

## 2. Sedimentation equilibrium

In this section, we briefly consider density profiles of colloidal fluids, characterized by the pair potentials (1) and (2), in

a constant gravitational or centrifugal field. Contrarily to atomic-size particles, the gravitational energy is easily comparable to the thermal energy, i.e. the ratio  $\alpha \equiv mg\sigma/k_B T$  is of order 1 where  $g$  is the gravitational acceleration and  $m$  is the buoyant mass of the colloidal particles. Provided the compressibility of the suspending fluid is negligible compared to the osmotic compressibility, one finds within the local density approximation (LDA) which is equivalent to local hydrostatic equilibrium that

$$\frac{dP(z)}{dz} = -mg\rho(z) \quad (3)$$

where  $P$  is the osmotic pressure of the isothermal suspension at altitude  $z$ .  $P$  is directly related to the equation of state (EOS)  $Z(\rho)$  as  $P(z) = \rho(z)k_B TZ(\rho(z))$ . The validity of the LDA was tested by extensive Monte Carlo (MC) simulations for  $0.1 \lesssim \alpha \lesssim 1$  for both HS and Yukawa systems by Barrat *et al.* [10]. Coarse grained density profiles were calculated by convoluting the local density with a resolution function of width comparable to  $\sigma$  in order to smooth out the oscillations at the bottom of the system due to layering. The MC data were in good agreement with the LDA assumption. More importantly, an inversion procedure was suggested, which allows to access the EOS which turns out to be rather sensitive to the exact form of the interparticle forces [10, 11]. If the profile  $\rho(z)$  is measured experimentally, one can integrate and invert (3) in order to obtain the EOS  $Z(\rho)$ . Hence density profiles could yield useful, though indirect information about the nature of the colloidal interaction. In the weak modulation limit  $\alpha \ll 1$ , thermodynamic perturbation theory leads to the linear response profile

$$\rho(z) = \rho_0 \left( 1 - \frac{\chi_T}{\chi_T^{id}} \frac{mgz}{k_B T} \right) \quad (4)$$

where  $\rho_0$  is the uniform density of the unperturbed suspension ( $\alpha = 0$ ),  $\chi_T$  is the osmotic compressibility and  $\chi_T^{id}$  its ideal limit ( $1/\rho_0 k_B T$ ) [10].

### 3. An *ab initio* description of counterion screening

A Statistical Mechanics description of charged colloidal systems usually starts from the so-called “primitive model” that involves the macroion and counterion degrees of freedom explicitly, assuming a combination of excluded volume and Coulombic interactions. The model is “primitive” insofar as the discrete structure of the solvent is completely neglected; the solvent just enters through its dielectric constant that reduce the bare Coulomb forces. Nevertheless it is still much too complicated to be analytically soluble and provides an *ab initio* basis for a theory or calculation of the macroion structure. The technical problem for solving the primitive model is the high asymmetry in charge of the macroions and counterions,  $Z/q \gg 1$ .

By brute force simulations, one may try to derive the macroion structure directly from the primitive model, which accounts explicitly for the discrete nature of the counterions. Such a calculation is feasible for  $Z/q \approx 20$  [12], but becomes rapidly untractable for higher asymmetries relevant for charged colloidal systems.

Secondly, one can use liquid structure integral equations for oppositely charged mixtures to predict the structure

from the primitive model. In general, similar problems arise for high asymmetries [13]. One interesting fact is that the mean spherical approximation (MSA) yields an effective macroion pair-potential that has the screened Coulomb form (2) but with a different renormalized charge  $Z^*$  that goes over to the DLVO charge in the limit of low macroion packing fraction  $\eta$ .

Another complementary density functional approach exploits the high asymmetry and the fact that the counterions follow quasi-instantaneously the macroion motions [14, 15]. This adiabaticity condition holds in fact rigorously in the limit of complete separation of time scales between the macro- and counterions. One then takes the counterion density field  $\rho_c(\mathbf{r})$  as a dynamical variable. The general strategy is a combination of density functional theory for the counterions and Molecular Dynamics for the macroions. Classical density functional theory for the one-component plasma of counterions is used to find the equilibrium density  $\rho_c(\mathbf{r})$  which depends parametrically on the macroion positions. With this density one calculates the Hellmann-Feynman forces, i.e. the counterion-induced forces between the macroions. In general, this force consists of many-body interactions of arbitrary order (non-linear screening). It is only for a density functional quadratic in the counterion density that the pairwise DLVO potential is recovered. The macroions are then moved according to this force and to their bare Coulomb repulsion, and this procedure is repeated many times in order to gather sufficient statistics for the macroions. The Car-Parrinello method [16] was used for the practical implementation of this procedure, together with a classical pseudopotential idea [14, 15]. Some of the results are shown in Figs 1–3, where the pair correlation function,  $g(r)$ , of the macroions is shown for three different thermodynamic states. The results based on pairwise effective

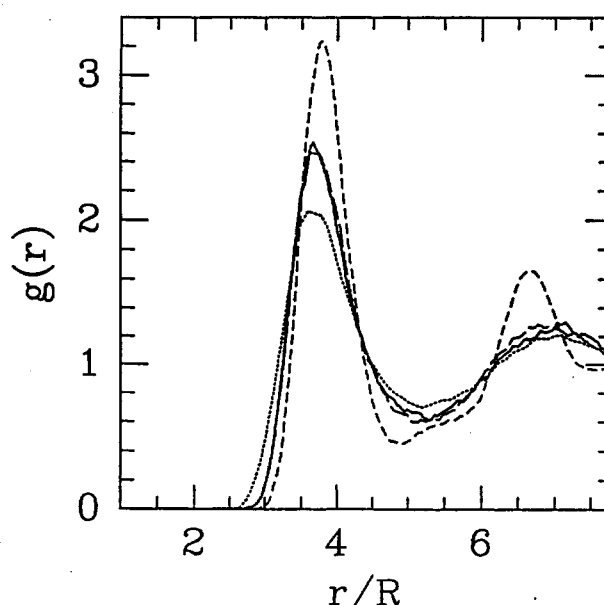


Fig. 1. Macroion-macroion pair correlation function  $g(r)$  vs. reduced distance  $r/R$ , where  $R \equiv \sigma/2$  is the macroion radius. The parameters are  $T = 300$  K,  $\epsilon = 78$  (water),  $R = 53$  nm,  $Z = 200$ ,  $\eta = 0.1$ . For these parameters, the colloidal system is a liquid. The full line is the data from the *ab initio* method. Furthermore results from a pairwise screened Coulomb potential are given. In particular, the corresponding data for the DLVO-model (long-dashed), the MSA (short-dashed) and the WSC-model (dotted) are shown

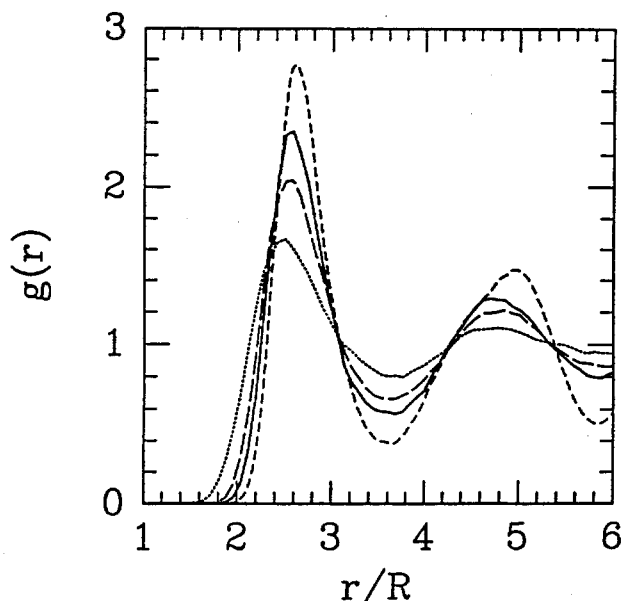


Fig. 2. Same as Fig. 1, but now for  $Z = 100$ ,  $\eta = 0.3$ . For these parameters, the colloidal system is also a liquid

tive potentials are shown for the DLVO-potential (2) (long-dashed line) and the MSA-potential (short-dashed line). The dotted line is the result of a screened Coulomb interaction model based on a Poisson-Boltzmann calculation for one macroion in a spherical Wigner-Seitz cell (WSC) [17]. It can be seen that the MSA generally overestimates while the WSC-model underestimates the structure. The traditional DLVO-potential works well for suspensions of low macro-

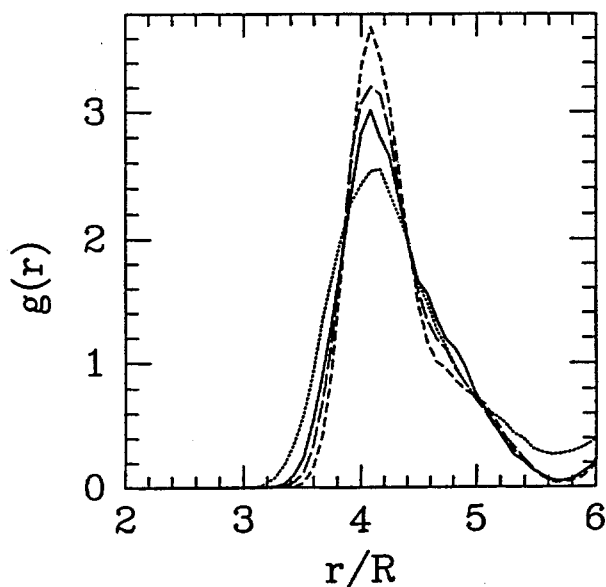


Fig. 3. Same as Fig. 1, but now for  $Z = 300$ ,  $\eta = 0.08$ . For these parameters, the colloidal system is a bcc-solid

ion density (Fig. 1), but fails for higher macroion packing fractions (Fig. 2), and overestimates the structure of the colloidal crystal (Fig. 3).

#### 4. Conclusions and perspectives

The first generalization of the *ab initio* description which is presently being considered is the strong screening regime with an added salt [15] where non-linear screening effects are expected to be more pronounced. The general scheme is also applicable to other inhomogeneous situations or low dimensionality systems [18]. This is presently under investigation. Another direction of important research is to clarify effects of polydispersity. One can also prepare well-defined bidisperse systems leading to interesting phase diagrams for these two-component colloidal alloys [19] that exhibit strong analogies with two-component mixtures of atomic liquids. Another extension of the density functional description of counterions may prove very useful to investigate linear polyelectrolytes, in particular the subtle interplay between bare and electrostatic persistence lengths.

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