EFFECTIVE FORCES BETWEEN COLLOIDAL PARTICLES

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Colloidal suspensions have proven to be excellent model systems for the study of condensed matter and its phase behavior [1]. Many of the properties of colloidal suspensions can be investigated with a systematic variation of the characteristics of the systems and, in addition, the energy, length and time scales associated with them allow for experimental probing of otherwise inaccessible regimes [2, 3]. The latter property also makes colloidal systems vulnerable to external influences such as gravity. Experiments performed in micro-gravity by Chaikin and Russell have been invaluable in extracting the true behavior of the systems without an external field [3]. Weitz and Pusey (private communication) intend to use mixtures of colloidal particles with additives such as polymers to induce aggregation and form weak, tenuous, highly disordered fractal structures that would be stable in the absence of gravitational forces.

Between any two colloidal particles, there is an attractive force caused by the interactions between the fluctuating dipole moments of their constituent atoms. This van der Waals force leads to irreversible aggregation of unprotected particles and it is desirable to diminish its magnitude [4] and provide a stabilization mechanism. Common mechanisms are steric stabilization [1]. For steric stabilization, colloidal particles are coated with polymers so that there is a short-range highly repulsive (nearly hard core) force between two colloidal particles when their respective polymer layers are compressed. We shall consider these types of colloidal particles later.

Charge stabilization occurs when charged surface groups on colloidal particles dissociate, ionizing the particle and emitting counterions into the solution. The standard theory of interaction in these charged colloidal suspensions is due to Derjaguin, Landau, Verwey and Overbeek (DLVO) [5] and the DLVO potential includes a non-negligible screened Coulomb repulsion

\[ U_{DLVO}(r) = \frac{Z^* e^2 \exp(-\kappa r)}{r} \]  

in addition to the short-range van der Waals attraction. The inverse Debye screening length, \( \kappa \), and the effective charge, \( Z^* \), are given by \( \kappa^2 = 4\pi \rho e^2/k_BT \epsilon \), \( Z^* = Z \exp(\kappa a)/(1 + \kappa a) \). Here, \( \epsilon \) is the dielectric constant of the solvent, \( \rho \) is the density of counterions, \( a \) is the radius of a colloidal "macroion", \( Z \) is its bare charge, \( k_B \) and \( T \) are the Boltzmann constant and temperature. The screened Coulomb potential is obtained in the mean-field linearized Poisson-Boltzmann approximation and is thus expected to have limited applicability, although the functional form of the potential with a renormalized charge has been argued to remain valid in a wider regime [6].

Indeed, the DLVO theory has been shown to explain some experimental data [7] but fails to account for others [8]. The main experimental challenges to the theory are numerous indications of a long-range attraction between colloidal particles. The latter are evident in experiments where particles are confined near a wall or in suspensions at higher densities. When two isolated particles at a low density have been considered, no attraction has been found. Hence, many-body effects might be thought to be responsible for this unexpected attractive force.

To study the role of confinement and evaluate many-body forces, we consider a system consisting of spherical colloidal macroions, a counterion density distribution \( \rho(\vec{r}) \) and a homogeneous solvent of a specified dielectric constant. The effective Hamiltonian for our system can be expressed as:

\[ \mathcal{H} = \frac{1}{2} \sum_i M_i \dot{\vec{R}}_i^2 + \sum_{i,j \neq i} U(|\vec{R}_j - \vec{R}_i|) + \mathcal{F}. \]  

\( M_i \) and \( \vec{R}_i \) are the masses and coordinates of the macroions and \( U(|\vec{R}_j - \vec{R}_i|) \) is the macroion-macroion interaction energy. In the expression for the free energy of the counterions [9, 10],

\[ \mathcal{F} = \int d^3\vec{r} \rho(\vec{r})(\phi_{ext} + \frac{1}{2} \phi_{int} + \phi_{id}(\rho) + \phi_{corr}(\rho)) \]  

we include: the macroion-counterion and counterion-wall interaction potentials, \( \phi_{ext} \); the Coulomb interactions between counterions, \( \phi_{int}(\vec{r}) = \int d^3\vec{r}' \frac{Z^* e^2}{|\vec{r} - \vec{r}'|} \); ideal gas, \( \phi_{id} \), and correlation, \( \phi_{corr} \), contributions. The ideal gas term is \( \phi_{id} = k_B T \log(\Lambda_B \rho(\vec{r})) - 1 \), where \( \Lambda_B \) is the de Broglie thermal wavelength and we employ the free energy of a one-component plasma [11] in evaluating \( \phi_{corr} \). We use pseudopotentials for macroion-counterion interactions [10] to suppress the large variation of the counterion density near a macroion core.
Given $P$, the forces between macroions due to counterions can be evaluated using the Hellmann-Feynman theorem. The total force acting on a macroion becomes:

$$ F_I = -\nabla_{\vec{r}_I} \mathcal{F}(\rho(\vec{r}), \phi_{ext}) - \nabla_{\vec{r}_I} \sum_j U((\vec{r}_J - \vec{r}_I)) \quad (4) $$

The equilibrium counterion density, $\rho(\vec{r})$, itself can be obtained from a functional minimization: $\frac{\delta \mathcal{F}}{\delta \rho} = 0$. An efficient scheme for solving a functional minimization of this type was developed by Car and Parrinello [12] in the context of quantum-mechanical electronic properties calculations and also used by Lowen, Madden and Hansen [10] for colloidal suspensions. Expressing the counterion density in terms of a wave function $\psi(\vec{r})$, $\rho(\vec{r}) = |\psi(\vec{r})|^2$, one can consider the Fourier components of $\psi(\vec{r})$, $\psi_k$, to be dynamical variables in a Lagrangian:

$$ L = \frac{1}{2} \sum_k m_k |\psi_k|^2 + \frac{1}{2} \sum_i \sum_j M_i \vec{R}_i \cdot \vec{F} - \sum_{i,j \neq i} U((\vec{R}_j - \vec{R}_i)) \quad (5) $$

with a constraint: $\int d^3 \rho(\vec{r}) = NZ$. $N$ is the number of macroions. $m_k$ are fictitious masses determining the time-scale of the dynamics of counterion density. We used this Lagrangian to solve the functional minimization by performing dynamical simulated annealing on $\psi_k$ to obtain the minimum of $\mathcal{F}$ for a fixed macroion configuration.

We started out with a configuration of two macroions in a periodic cubic box of length $1\mu m$ at a temperature $T = 300K$ in water, $\epsilon = 78$. The counterion density was evaluated on a $96^3$ grid and the radius and charge of a macroion were $a = 100nm$ and $Z = 200e^-$ ($e^-$ stands for the elementary charge). The forces between macroions at a series of different separations were measured. At this low packing fraction, relatively low surface charge and counterion concentration, the DLVO pair-potential between two macroions is expected to hold. We plot the DLVO prediction for the periodic system in Fig. 1. We show our density functional minimization results in the same figure as well as the force resulting from an optimal fitting to a pair-potential of the DLVO form. The numerical values for the inverse screening length and effective charge for the optimal fit are presented as the first set in Table 1.

In order to check the validity of pair-wise additivity that we had tacitly assumed above, we placed three colloidal particles in a unit cell with periodic boundary conditions. Maintaining our previous pseudopotential parameters, we studied the following geometries. First, we positioned the three macroions in configurations of equilateral triangles of different sizes and calculated the force on one of the macroions as a function of the edge of the triangle. In Fig. 2, we plot our data for the force in these configurations as a function of the distance and compare it to the force obtainable from an additive pair-potential. Secondly, we also placed the three macroions in an asymmetric triangular configuration where two macroions were close to each other (separation of 200nm) and a third macroion was at a distance of 473nm from either of the two. We measure a force of $1.24 \times 10^{-2} (e^-/nm)^2$ on the first macroion while pairwise additive forces predict $1.22 \times 10^{-2} (e^-/nm)^2$ for the value. Thus, we detect no three-body component in the effective forces.

To study forces between macroions in a confined system, we introduced two parallel short-range repulsive walls. We placed the macroions at different separations and distances from a wall and measured the effective forces between them. We fit our data to a DLVO-type force and the effective parameters obtainable from the fit are summarized in Table 1. Our results can be understood as follows. The introduction of repulsive walls increased the counterion density in the middle of the simulation cell, while decreasing the Debye screening length in that region (compare sets 1 and 2 in the table). On the other hand, near the walls,
Table 1: The parameters corresponding to the optimal effective pair interaction potential between macroions in different geometries. The first set of data was obtained with periodic boundary conditions while walls were introduced in the last three. $R_x$ measures the distance from a wall. $\kappa a$ and $Z^*$ are obtained from the fit, the bare charge $Z$ is calculated from $n_a$ and $Z'$. The DLVO prediction for a periodic system is: $Z = 200$, $Z^* = 205.8$ and $\kappa a = 0.258$.

![Image of Table 1]

Figure 2: Test of the additivity of the effective macroion potential. Three macroions were placed in equilateral triangular configurations and the force on a macroion as a function of the edge of the triangle was measured. Open circles are our data whereas the solid line indicates the force from an additive DLVO-type potential with the parameters: $Z^* = 212.5 e^-$, $\kappa a = 0.374$. The force is scaled to $(e^-/nm)^2$.

![Image of Figure 2]
Figure 3: The depletion force as a function of the distance between two hard spheres in a mixture of other hard spheres of the same size at a packing fraction $\phi = 0.45$. The distance is measured in hard sphere diameters, $\sigma$, and the force is scaled to $k_B T/\sigma$.

in a hard-sphere fluid derived from a pair-correlation function using Eq. (7) is given in Figure 3. At a packing fraction of $\phi = 0.45$, it suffices to consider 108 hard spheres in a cubic box with periodic boundary conditions to obtain the first features in the force profile. We can prove the validity of our calculation by measuring the depletion force directly by recording the total momentum transfer in a unit time on a sphere at a known distance from another one. We compare both of those force measurements to the AO prediction in Figure 3.

Similarly, the depletion force between a sphere and a wall can be obtained from the density profile:

$$F/k_B T = \frac{\partial \ln(\rho(x))}{\partial x}$$

where $x$ is the direction perpendicular to the wall and $\rho(x)$ is the local density of the hard sphere fluid. The well-known layering of fluid molecules near a wall leads again to a more complex structure for the force than AO predicts. See Fig. 4 for the force data and the AO prediction. We also plot the force obtained from momentum transfer measurements. The data was obtained with the same number of spheres at the same density as before.

Depletion forces in complex geometries with step edges and non-trivial curvature have been measured and argued to have profound consequences for cellular biology or entropic control and directed motion of colloidal particles. The AO-type calculations of entropic forces and potentials in these geometries are simple enough to carry out while more precise predictions quickly become rather laborious and, to our knowledge, have not been attempted. To go beyond the AO theory, we calculated entropic forces and potentials for a system of 324 hard spheres at a packing fraction of about 0.45 in a three-dimensional T-shaped channel. Potentials near step-edges and corners are of principal interest and are shown in Figure 5. A comparison with the AO prediction is also shown in the figure. The potential barrier repelling a hard sphere from a step-edge is simply a reflection of the density decrease near it. Analogously, the potential minimum attracting particles towards a corner and the sharp increase in density there are different manifestations of the same effect.

There is an interesting and important feature to the depletion forces that already manifests itself in the AO approach. Depletion forces need not be pairwise additive. In the AO approximation, the force between two particles arises from the overlap of excluded volumes. Three-body effects become relevant when the hard spheres are considered in configurations in which their pairwise overlap volumes themselves overlap, resulting in an over-counting of the actual overlap volume. An example could be a triangular configuration. The AO prediction for an equilateral configuration is calculable.
For the packing fraction $\phi = 0.45$, the AO two-body force at two sphere contact is $F_{AO} = -2.0 \frac{k_B T}{\sigma}$. If forces were additive, the magnitude of the total force on a sphere in this triangular configuration would be $2F_{AO} \cos(\pi/6) = -3.5 \frac{k_B T}{\sigma}$. Instead, when all overlap volumes are correctly accounted for, an AO-like analysis predicts instead a force of $-2.9 \frac{k_B T}{\sigma}$. The exact three-body force can in principle be found from a three-point correlation function but obtaining reliable statistics for this measurement is rather time consuming. Instead, we prepared the described triangular configuration and measured the momentum transfer on each of the spheres in a simulation. The two-body force at contact for $\phi = 0.45$ is $F_{sim} = -6.8 \frac{k_B T}{\sigma}$ (see Fig. 3). The actual measured force, $-10.0 \frac{k_B T}{\sigma}$, is again significantly lower than the additive pairwise force: $2F_{sim} \cos(\pi/6) = -11.8 \frac{k_B T}{\sigma}$. Indeed, the three-body component in this geometry for our system of hard spheres is a significant percentage of the total force.

In conclusion, we have performed calculations of effective forces between charged colloidal particles in different configurations and studied effective depletion forces in hard sphere colloids. In the first case, our data are well fit to screened Coulomb type potentials. It should be noted that in our calculations, the walls were not charged and dielectric discontinuities between the suspension and the walls were not considered. One may speculate that long-range attraction cannot be accounted for by static calculations and that they probably originate from temporal fluctuations. In the second case, a comparison of our numerical data and the Asakura-Oosawa theory indicates that the AO theory underestimates the magnitude of depletion forces at contact, ignores the complex nature of entropic interactions, consisting of several maxima and minima and underestimates the range of the interactions.

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REFERENCES


[4] The magnitude of van der Waals forces can be reduced by index matching the solvent and the particles but this is unfortunately incompatible with density matching. A micro-gravity environment is thus essential to avoid sedimentation and resulting complications.


