Long-range Attraction between Like-charged Colloids

EXECUTIVE SUMMARY

Among the soft matter systems, charge-stabilized colloidal suspensions (e.g., submicron sized polystyrene latex and silica particles dispersed in water) have gained recognition as tremendously useful model condensed matter systems because of their structural ordering and rich phase behavior. Hence, these systems are of considerable interest to study fundamental questions, which are also relevant for atomic systems. Understanding of this simple model system is far from complete with respect to the effective pair-potential \( U(r) \) between the charged colloids arising due to the basic electrostatic interactions among the constituents. Using a confocal laser scanning microscope we probe charged latex suspensions and show that \( U(r) \) between like-charged particles exhibits a long-range attractive minimum when effective charge density of the particles is quite high. We also observe stable bound pairs. These observations provide a direct and unequivocal evidence for long-range attraction between like-charged colloidal particles.

OUTLINE

For a very dilute suspension, the pair-correlation function \( g(r) \) is directly related to the effective pair-potential \( U(r) \) by

\[
g(r) = \exp\left[-\frac{U(r)}{k_B T}\right] \quad (1)
\]

Hence, \( U(r) \) can be obtained by measuring \( g(r) \). Digital video microscopy and optical tweezer techniques have been used in the past to measure \( g(r) \) by imaging the colloidal particles. However, only the particles close to the microscope cover-glass could be imaged in these studies because of the limited depth of focus. The cover-glass has strong influence on \( U(r) \). Further, the attraction observed in these experiments is attributed to imaging artifacts and projection errors. Thus, to date, there is no direct experimental evidence for existence of a long-range attractive term in the \( U(r) \) of like-charged colloids in a bulk suspension with monovalent counterions.

Observation of long-range attraction in very dilute bulk suspensions requires setting-up right experimental conditions: (a) Particles of high effective charge density, are essential to increase the strength of attraction as well as to increase the counterion concentration in the medium, which mediate the attraction between like-charged particles (b) Elimination of wall effects and (c) Avoiding sedimentation of particles due to gravity. We have selected highly charged polystyrene colloidal particles among our stock of synthesized suspensions to increase the concentration of counterions and redispersed in a density-matched fluid (50:50 H\(_2\)O-D\(_2\)O mixture) to eliminate sedimentation due to gravity. The effect of charged wall is eliminated by employing a confocal laser scanning microscope for imaging the particles far away (> 200 \( \mu \)m) from charged cover slip. We minimize the impurity ion concentration by completely deionizing the suspension using mixed-bed ion-exchange resins.

We view the colloidal particles deep inside the suspensions with a fast (7.3 frames/sec) scanning CLSM to obtain two dimensional (2D) optical slices. We record several thousands of images as time series and several such series from different locations in the sample. We obtain in-plane \( g(r) \) (by determining the positions of the particles by image analysis in each frame, and then averaging over several thousands of such frames. The \( U(r) \) is obtained from the measured \( g(r) \) using Eq. 1. To establish that this methodology is free from imaging artifacts we first reproduce the standard result by preparing a very dilute deionized suspension (volume fraction \( \phi = 0.0001 \), and diameter \( d = 780 \, nm \) of latex particles of low surface charge density \( \sigma = 0.004 \, \mu C/cm^2 \). We observe only individual particles (Fig. 1A) undergoing Brownian motion and the \( U(r) \) (Fig. 1B) obtained from measured \( g(r) \) is found to be screened Coulomb repulsive and fits to the potential form given by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. In dilute suspension of high charge density (\( \sigma = 2.7 \, \mu C/cm^2 \)) latex particles we observe stable bound pairs and higher order particle clusters (Fig. 2). These observations provide direct evidence for existence of long-range attraction between like-charged colloids.

![Fig. 1](image1.png) A: Confocal image of 780 nm polystyrene particles of low charge density. B: Pair-potential \( U(r) \) obtained from measured pair-correlation function \( g(r) \) shows screened Coulomb repulsion between like-charged particles

![Fig. 2](image2.png) Confocal images of 600 nm polystyrene particles of high charge density showing (A) bound pairs and (B) three, four and five particles
**CHARGE STABILIZED COLLOIDS**

Monodisperse particles having a size in the range of 1 nm to 1 μm when dispersed in a polar solvent execute Brownian motion and are known as colloidal suspensions. When two particles approach distance of the order of a nanometer or less, particles experience van der Walls attraction. This leads to flocculation and make these suspensions unstable. Stable suspensions are prepared by charging the particles during the synthesis. This is known as charge stabilization. In a charge stabilized suspension, the particles (e.g., polystyrene) are negatively charged with H⁺ ions as counterions. Counterions screen the repulsive Coulomb interaction between the particles.

**LONG-RANGE ATTRACTION**

Existence of stable bound pairs implies an attractive minimum $U_m$ with magnitudes of the order of thermal energy $k_b T$ or more in the pair-interaction $U(r)$ between the like-charged particles. The magnitude of $U_m$ and the interparticle distance $R_m$ at which this attractive minimum occurs, have been measured by obtaining $U(r)$ using Eq. (1). The $g(r)$ and $U(r)$ for two samples with charge densities $\sigma = 2.7$ and $0.3 \mu C/cm^2$ are shown in Fig. 3. The pair-potential $U(r)$ clearly shows an attractive minimum (Fig. 3) at an interparticle distance of about 1.45 μm which is really long-ranged as it corresponds to about 2.4 times the diameter ($d=600$ nm) of the particles. Further, the well depth (Fig. 3) is found to be larger ($U_m = 1.82 k_b T$) for particles of $\sigma = 2.7 \mu C/cm^2$ as compared to that for particles with $\sigma = 0.3 \mu C/cm^2$. Measured experimental $U(r)$ data was found to fit to the following empirical expression $U(r) = A \exp(-r/\lambda) - B \exp(-r)$, where the constants $A$, $B$ represent the strength of repulsive and attractive components of the interaction, respectively and $\kappa$ represents the range of interaction.

Our measurements thus confirm the existence of a long-range attractive term in the effective pair-potential between like-charged colloids. The monovalent counterion (H⁺ ions) concentration is increased in the system by increasing the charge density on the particles. The attraction is believed to arise from the counter ions mediation between the macro ions.

**MODELS APPLIED**

For suspensions of low charge density particles the counterion concentration is much smaller than salt ion concentration. Under these conditions DLVO theory is expected to provide an accurate description of the pair-interaction between charged colloids, and we indeed obtain the DLVO potential $U(r) = A \exp(-r/\lambda) - B \exp(-r)$ from our analysis of the experimental data (Fig. 1B). The fitted values of the Coulomb potential strength $A$ and the inverse Debye screening length $\lambda$ are found to be reasonable. For suspensions of charge density particles the counterion concentration is much higher than the salt concentration. Under these conditions the DLVO theory fails. The experimental $U(r)$ (Fig. 3) is found to fit to an empirical expression $U(r) = A \exp(-r/\lambda) - B \exp(-r)$, where the constants $A$, $B$ represent the strength of repulsive and attractive components of the interaction. This form resembles Sogami-Ise pair-potential.

**ACHIEVEMENT**

For the first time, we observed stable bound pairs using a CLSM. By detailed quantitative image analysis of confocal images we find that the measured $U(r)$ has a long-range attractive component with well depths larger than $k_b T$. These observations provide a direct and unequivocal evidence for the existence of long-range attraction in $U(r)$ of like-charged colloidal particles.

**PUBLICATIONS ARISING OUT OF THIS STUDY AND RELATED WORK**


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