Direct Measurement of Three-Body Interactions amongst Charged Colloids

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Three-body interactions amongst three charged colloidal particles are measured in a deionized aqueous solution. Two of the particles are confined to an optical line trap while the third one is approached by means of a focused laser beam. From the observed particle configurations we extract the three-body potential which is found to be attractive and roughly of the same magnitude and range as the pair interactions. In addition, numerical calculations are performed which show qualitative agreement with the experimental results.

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Precise knowledge of the particle interaction is the basis for understanding the thermodynamic properties of condensed matter. Typically these interactions are dealt with in a pairwise fashion, but if the governing physical equations are nonlinear, interactions between two particles can be modified by a close third or fourth particle. The total energy is then no longer given by the sum of all pair potentials alone, but additional many-body interactions appear. Systems in which many-body interactions are important include electron screening in metals [1], island formation on surfaces [2], chemical processes in solids [3], and even noble gases [4–6]. Until now no direct measurement of many-body interactions has been performed, mainly for the reason that more positional information is required than is available on the level of pair-correlation functions and structure factors usually determined in atomic systems.

In contrast to atomic systems, it is possible in colloidal systems to experimentally follow individual particle trajectories, which can then be further processed to evaluate the interaction potentials between the particles. Additionally colloidal interactions can be tuned over a wide range, simply by changing the salt concentration (in contrast to atoms where interactions are unchangeably dictated by their electronic structure). At sufficiently small salt concentrations, the interaction range can reach several μm. These properties of colloidal systems have been repeatedly exploited by a number of groups: In highly diluted systems with experimental conditions similar to this work, the pair interaction between charged colloids has been experimentally determined [7], showing fine agreement with theoretical predictions [8]. Yet, this does not apply to denser suspensions. If more than two colloids are within their interaction range, the simple pairwise description breaks down and many-body interactions occur, as has been shown in recent computer simulation studies [9–11] and experiments [12]. Hence colloidal suspensions represent an ideal model system for systematic investigations of many-body interactions.

This Letter reports a direct measurement of the interaction among three charged colloidal particles, similar in spirit to the earlier experimental studies on two-particle interaction potentials [7]. Two of the particles were confined by means of a scanned laser tweezer to a quasistatic line-shaped optical trap in which they diffused due to thermal forces. A third particle was localized in a point-like laser tweezer at distance d (see inset of Fig. 1). When this third particle was approached to the line trap, significant deviations from pairwise additivity were observed. This experimental finding is also supported by the additionally performed Poisson-Boltzmann calculations.

We used a highly diluted aqueous suspension of charge-stabilized silica spheres (990 nm diameter), which has been confined in a silica glass cuvette with 200 μm spacing. The cuvette was connected to a standard deionization circuit described elsewhere [13]. Before each measurement the water was pumped through the ion exchanger and typical ionic conductivities below

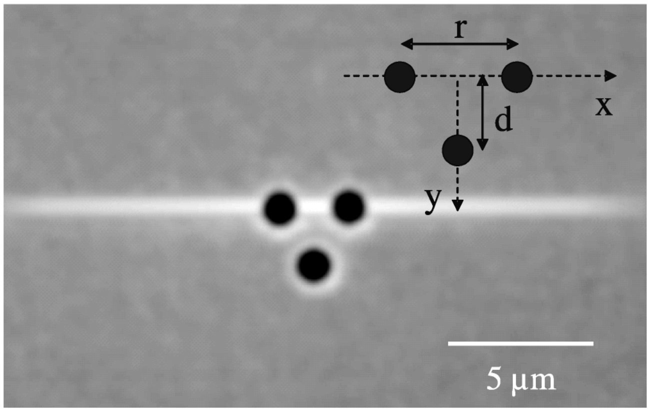

FIG. 1. Photograph of a sample cell with two silica particles confined to a light trap created by an optical tweezers and a third particle trapped in a focused laser beam (view from the top). The third particle is located on the midline between the other two particles, a distance d apart from the laser line trap. The inset shows schematically the experimental geometry.

0.07 μS/cm were obtained. After the suspension was injected, the cuvette was disconnected from the circuit during the measurements. This procedure yielded stable and reproducible ionic conditions during the experiments.

Particle interaction measurements were performed with scanned optical tweezers, a technique which has been introduced and characterized in detail by Yodh and co-workers [14]. Therefore this technique is described here only briefly. The focused beam of an Ar^+ laser (488 nm) was scanned across our sample cell by means of a galvanostatically driven mirror with a frequency of about 350 Hz to create a Gaussian intensity distribution. The half-widths of this laser line along and perpendicular to the scanning direction were chosen to be $\sigma_x \approx 4.5$ μm and $\sigma_y \approx 0.5$ μm, respectively. All particles are located in a plane about 0.5 μm above the bottom of the glass cuvette. Because of the negatively charged silica substrate, the particles experience a repulsive vertical force balanced by the particle weight and the vertical component of the light force. As the potential in the vertical direction is much steeper than the in-plane laser potential, the effect of vertical particle fluctuations can be disregarded, as verified by additionally performed computer simulations. The particles were imaged with a long-distance, high numerical aperture microscope objective onto a CCD camera and the lateral positions of the particle centers were determined with a resolution of about 25 nm by a particle recognition algorithm.

First a single particle was inserted into the trap. The Brownian motion of the particle was recorded and from these data its positional probability distribution $P(x, y)$ was determined. The laser potential $u_L(x, y)$ is directly obtained via the Boltzmann distribution $P(x, y) \propto e^{-\beta u_L(x,y)}$, where β^{-1} corresponds to the thermal energy. Next, we inserted a second particle in the trap. The four-dimensional probability distribution is now $P(x_1, y_1, x_2, y_2) = P_{12} e^{-\beta[u_L(x_1,y_1)+u_L(x_2,y_2)+u_{12}(r)]}$ with x_i, y_i being the position of the ith particle relative to the laser potential minimum and $u_{12}(r)$ the distance-dependent pair-interaction potential between the particles. Since it is reasonable to assume that the pair interaction depends only on the particle distance, we projected $P(x_1, y_1, x_2, y_2)$ onto a one-dimensional distance distribution $P(r)$. From the measured $P(r)$ we obtained the total potential energy of the particles and after subtracting the external laser potentials we were left with the pair-interaction potential $u_{12}(r)$.

The pair-interaction potential between two charge-stabilized particles is given by the Yukawa potential [8]

$$\beta u_{12}(r) = (Z^*)^2 \lambda_B \left(\frac{\exp(\kappa R)}{1 + \kappa R}\right)^2 \frac{\exp(-\kappa r)}{r}, \qquad (1)$$

where Z^* is the effective (or renormalized) charge [15] of the particles, λ_B the Bjerrum length in water at room temperature, κ^{-1} the Debye screening length (given by the salt concentration), R the particle radius, and r the center-center distance between the particles. Figure 2 shows the experimentally determined pair potential (symbols) together with a fit to Eq. (1) (solid line). As can be seen, our data are well described by Eq. (1). As fitting parameters we obtain $Z^* \approx 6500$ electron charges and $\kappa^{-1} \approx 470$ nm. Z^* is in good agreement with the predicted value of the saturated effective charge of our particles (about 6900 for water at room temperature [16]) and κ^{-1} agrees reasonably with the bulk salt concentration in our suspension as obtained from the ionic conductivity. Given the additional presence of a charged substrate, it might seem surprising that Eq. (1) describes our data successfully. However, it has been demonstrated experimentally [7] and theoretically [17] that a Yukawa potential captures the leading order interaction also for colloids close to a charged wall. A single confining wall introduces only a weak perturbation of about $0.1 k_B T$ which is below our experimental resolution; see Fig. 2. Repeating two-body measurements with different laser intensities (50 to 600 mW) yielded within our experimental resolution almost identical pair-potential parameters. This clearly demonstrates that the possibility of light-induced particle interactions (e.g., optical binding [18]) can be safely ruled out.

In a last step, we pinned a third particle by means of an additional pointlike laser trap at a distance d along the perpendicular bisector of the scanned laser line (cf. Fig. 1), where it was localized during the whole measurement. We carefully checked that the empty point trap (i.e., the trap without the third particle) had no influence on the pair-interaction potential between the particles in the line tweezers. Repeating the three-body measurement with different laser intensities for both the laser line and the point trap led to similar results, again ruling out intensity-dependent effects. From the distance

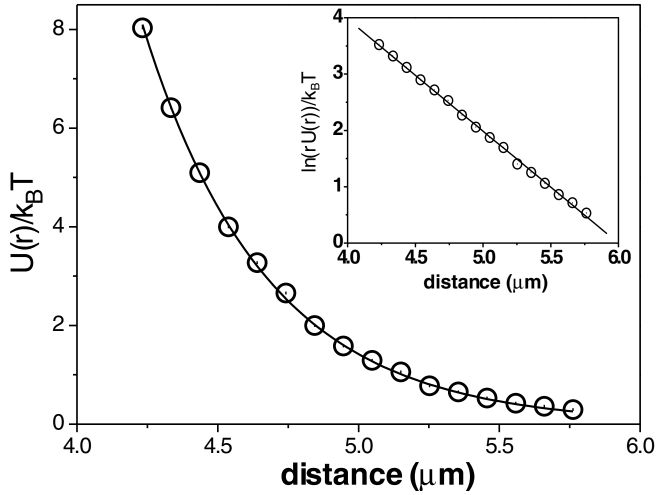

FIG. 2. Measured pair-interaction potentials (symbols) in the absence of the third particle. The data agree well with a Yukawa potential (solid line). In the inset the potential is multiplied by r and plotted logarithmically, so that Eq. (1) transforms into a straight line.

distribution of the two particles in the laser trap, we can, applying the same procedure as in the two-particle measurement, extract the total interaction energy which is now dependent also on the distance d , i.e., $U = U(r, d)$. Following the definition of McMillan and Mayer [19], the total interaction energy for three particles $U(r, d)$ can be written as

$$U(r, d) = u_{12}(r_{12}) + u_{13}(r_{13}) + u_{23}(r_{23}) + u_{123}(r_{12}, r_{13}, r_{23}) \tag{2}$$

with u_{ij} being the pair potential between particles i and j as given in Eq. (1) and shown in Fig. 2, and u_{123} the three-body interaction potential. r_{12}, r_{23}, and r_{13} are the distances between the three particles which due to the chosen symmetric configuration can be expressed by just two variables, $r = r_{12}$ and d.

The measured interaction energies $U(r, d)$ are plotted as symbols in Fig. 3 for several distances of the third particle ($d = 4.1, 3.1, 2.5, 1.6$ μm). As expected, $U(r, d)$ becomes larger as d decreases due to the additional repulsion between the two particles in the trap and the third particle. In order to test whether the interaction potential can be understood in terms of a pure superposition of pair interactions, we first calculated $U(r, d)$ according to Eq. (2) with $u_{123} = 0$. This was easily achieved because the positions of all three particles were determined during the experiment and the distance-dependent pair potential is known from the two-particle measurement described above (Fig. 2). The results are plotted as dashed lines in Fig. 3. Considerable deviations from the experimental data can be observed, in particular, at smaller d. These deviations can be explained only if we take three-body interactions into account. At the largest distance, i.e., $d = 4.1$ μm, our data are well described by a sum over pair potentials which is not surprising, since the third particle, being that far away, cannot influence the interaction between the other two. In agreement with theoretical predictions [9,10], the three-body interactions therefore decrease with increasing distance d.

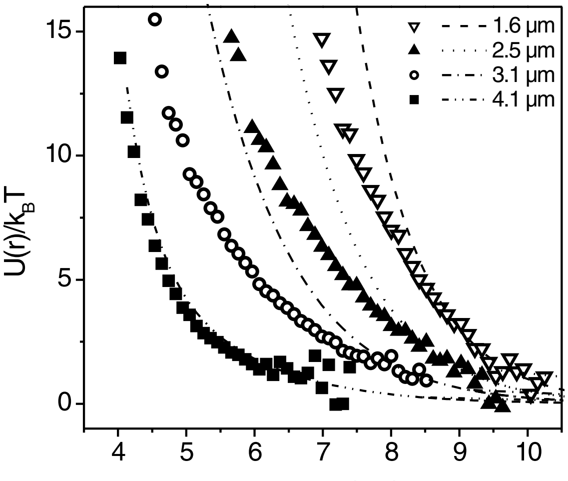

FIG. 3. Experimentally determined interaction energy $U(r)$ (symbols) for two particles in a line tweezers in the presence of a fixed third particle with distance d on the perpendicular bisector of the line trap. For comparison the superposition of three pair potentials is plotted as lines. Symbols and lines are labeled by the value of d.

According to Eq. (2) the three-body interaction potential u_{123} is simply given by the difference between the measured $U(r, d)$ and the sum of the pair potentials, i.e., by the difference between the measured data and their corresponding lines in Fig. 3. This difference is plotted as symbols in Fig. 4. It is seen that u_{123} is entirely attractive and becomes stronger as the third particle is approached. The range of u_{123} is of the same order as the pair-interaction potentials. To support our results, we also performed Poisson-Boltzmann (PB) calculations in a similar way as in [10]. The PB theory provides a mean-field description in which the microions in the solvent are treated as a continuum, neglecting correlation effects between the microions. It has repeatedly been demonstrated [20,21] that in the case of monovalent microions the PB theory provides a reliable description of colloidal interactions. We used the multicentered technique, described and tested in other studies [11] to solve the nonlinear PB equation for the electrostatic mean-field potential Φ, which is related to the microionic charge density $\rho_c = -(\kappa^2/4\pi\lambda_B)\sinh\Phi$. From these ion distributions one can compute the force acting on each particle. For details see [22]. Calculating the force, and from it the pair potential, between only two particles, we first reproduced the measured pair interaction in Fig. 2. The

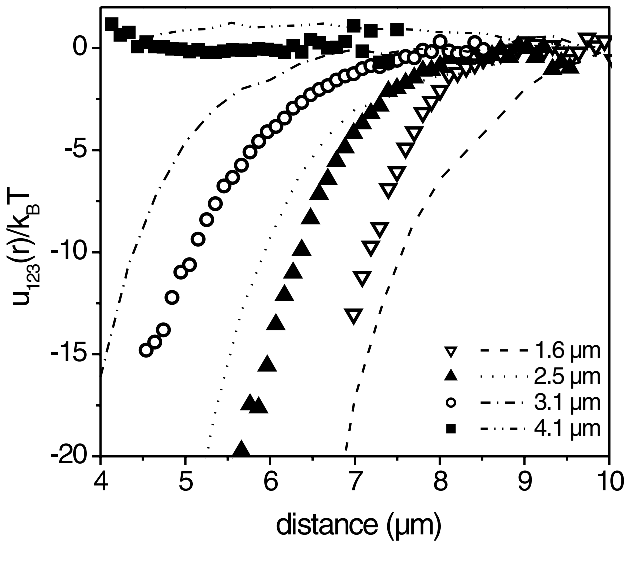

FIG. 4. Three-body potentials for different d. Measured three-body potentials are indicated by symbols. The lines are three-body potentials as obtained from the solution of the nonlinear Poisson-Boltzmann equation for three colloids arranged as in the experiment. The parameters in the Poisson-Boltzmann calculation were chosen such that the pair-interaction potentials were correctly reproduced. Symbols and lines are labeled by the value of d.

calculation of three-body potentials was then carried out by calculating the total force acting on one particle in the line trap and subtracting the corresponding pair forces obtained previously in the two-particle calculation. The difference has been integrated to obtain the three-body potential. The results are plotted as lines in Fig. 4 and show qualitative agreement with the experimental data. The remaining deviations are explained by (i) the limited accuracy to which the depth and shape of the laser line trap can be determined, (ii) the simplifying assumption made in the PB calculation that the three colloidal spheres are identical, and by (iii) neglecting substrate effects in the PB calculations. Although the wall effect is likely to be very small (probably even smaller than the already minute effect of the substrate on the pair potential, see discussion above), it cannot be ruled out completely. This point certainly needs further theoretical consideration. Given the above uncertainties, the agreement between experiment and calculations is reasonable, in particular, with respect to the sign, amplitude, and range of the three-body interaction potential. This strongly supports our interpretation of the experimental results in terms of three-body interactions.

We have demonstrated that in the case of three colloidal particles, three-body interactions present a considerable contribution to the total interaction energy and should therefore be taken into account. Whenever dealing with systems comprised of many (much more than three) particles, in principle also higher-order terms have to be considered. We expect, however, that there is an intermediate density regime, in which the macroscopic properties of systems can be successfully described by taking into account only two- and three-body interactions. Indeed, there are systems where this was experimentally observed [2,5]. At even larger particle densities n-body terms with $n > 3$ have to be additionally considered, which may partially compensate. Even in this regime, however, many-body effects are not canceled, but may lead to notable effects, e.g., to a shift of the melting line in colloidal suspensions, as recently demonstrated by PB calculations [11].

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