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Effective Interactions in Mixtures of Silica Microspheres and Polystyrene Nanoparticles

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We investigate the effect of small concentrations of highly charged nanoparticles on the stability of uncharged colloidal microspheres using large-scale simulations. Employing pair potentials that accurately represent mixtures of silica microspheres and polystyrene nanoparticles as studied experimentally,[1] we are able to demonstrate that nanoparticle-induced stabilization can arise from a relatively weak van der Waals attraction between the colloids and nanoparticles. This demonstrates that the nanoparticle haloing mechanism[2] for colloidal stabilization is of considerable generality and potentially can be applied to large classes of systems. The range of optimal nanoparticle concentrations can be tuned by controlling the attraction between colloids and nanoparticles.

Several years ago, a new colloidal stabilization mechanism referred to as nanoparticle haloing was reported.[2,3] In these experiments, it was observed that small volume fractions of highly charged zirconia nanoparticles are able to stabilize silica microspheres. The remarkable aspect of this phenomenon is that the nanoparticles counteract the van der Waals attraction between the silica colloids, even though control measurements explicitly ruled out a strong adsorption of the nanoparticles on the microsphere surfaces. By employing a Monte Carlo (MC) method that is capable of explicit calculations for fluid mixtures with large size asymmetries,[4,5] Liu and Luijten have been able to demonstrate that these observations can be explained from a *weak* colloid−nanoparticle attraction,[6,7] causing the formation of a shell of nanoparticles that results in an effective colloidal repulsion. By careful choice of the computational parameters, (semi)quantitative agreement could be obtained between the experiments and the calculations, including an explicit prediction for the effect of size asymmetry.[8] Simultaneously, analytical calculations based upon an integral-equation approach[9] demonstrated that electrostatic repulsions between the nanoparticles alone (i.e., in the absence of a colloid−nanoparticle attraction) can also cause their segregation to the surface of the negligibly charged microspheres, albeit at a considerably larger Debye screening length (lower salt concentration) than employed in the actual experiments. A second phenomenon that is observed upon the addition of sufficiently high concentrations of nanoparticles is reentrant gelation, which is ascribed to depletion attraction between the colloids.[2] Both computational[6] and analytical[9] approaches have recovered this attraction, but with clear deviations from the standard Asakura−Oosawa behavior.[10] Indeed, given the strongly nonadditive nature of the various pairwise interactions in this binary mixture,[11] care must be exercised when interpreting the nature of depletion-induced interactions.

The potential impact of this new colloidal stabilization technique makes it highly desirable to demonstrate its general applicability and to obtain a more complete understanding. The complex solution chemistry in the original experiments[2,3] made it difficult to characterize the colloidal interactions accurately. Because these interactions provide the starting point for particle-based simulations, it is thus of great interest that Chan and Lewis have recently performed experiments on binary mixtures that have a similar size and charge asymmetry but for which the interactions are better characterized.[1] In the new experimental work, the zirconia nanoparticles are replaced by polystyrene particles, and three different systems are investigated. Two cases, namely, negatively charged colloids (silica at pH 5) with either cationic amidine polystyrene or anionic sulfate polystyrene nanoparticles, exhibit unsurprising behavior. In these systems, there is either a strong attraction or a strong repulsion between colloids and nanoparticles, resulting in strong adsorption or virtually no adsorption. Without adsorption, the silica microspheres are stabilized by their direct electrostatic repulsion, whereas the strongly adsorbing case leads to "bridging" flocculation. The third and most interesting case corresponds to weakly charged colloids (pH 3, zeta potential $\zeta_{\text{micro}} = -1$ mV) with sulfate polystyrene nanoparticles ($\zeta_{\text{nano}} = -120$ mV). Under these conditions, the electrostatic interaction between the microspheres is overwhelmed by their van der Waals attraction. Nevertheless, stabilization is observed in the presence of nanoparticles. This is particularly remarkable because the electrostatic colloid−nanoparticle interaction is expected to be negligibly small and measurements indeed indicate only weak adsorption of the nanoparticles to the microsphere surface. It is the purpose of this letter to investigate this system by means of large-scale computer simulations in order to explain the experimental observations and clarify their relation to the original nanoparticle haloing observations.

We adopt the following model system. Both the colloidal microspheres and the nanoparticles are modeled as hard spheres, with respective diameters of $\sigma_{\text{micro}} = 1.18\ \mu$m and $\sigma_{\text{nano}} = 19$ nm. In addition to the hard-sphere potential, the nanoparticles have an electrostatic repulsion V_{nano}, and the microsphere−nanoparticle interaction $V_{\text{m-n}}$ consists of a van der Waals attraction and a weak electrostatic repulsion. All potentials are calculated

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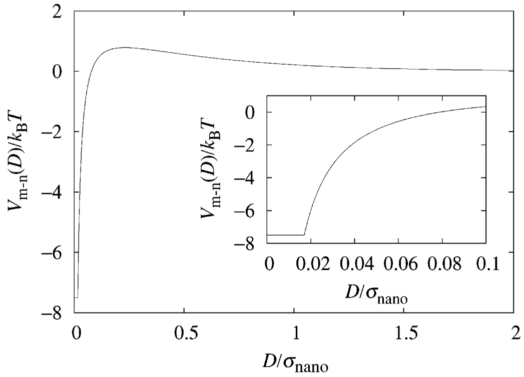

Figure 1. Colloid−nanoparticle potential resulting from a van der Waals attraction and a weak electrostatic repulsion as a function of surface separation D (measured in units of small-particle diameter σ_{nano}). In this example, the minimum in the potential is truncated at $-7.5k_BT$. The inset shows a magnified view near contact. All potential values that would be lower than V_{cut} are set to V_{cut}, which causes a small flat region for separations of less than a few percent of the nanoparticle diameter. In the simulations, the potential is set to zero for separations larger than $D = 13.5\sigma_{\mathrm{nano}}$.

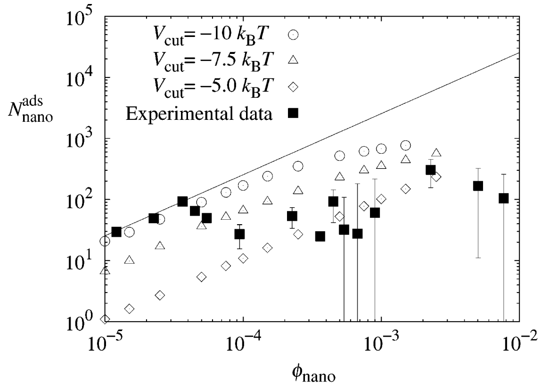

Figure 2. Surface coverage (in units of adsorbed nanoparticles per microsphere) as a function of nanoparticle concentration for different values of the potential well cutoff V_{cut} (cf. Figure 1). The filled symbols represent the experimental data,[1] and the solid line represents 100% nanoparticle adsorption. The uncertainty in the numerical data is negligibly small on the scale of this plot. As the magnitude of the potential-well cutoff is increased, the degree of adsorption increases accordingly.

as outlined in the Supporting Information of ref 1. The solvent and salt are modeled implicitly as a dielectric continuum, leading to screened electrostatic interactions that are obtained via the linear superposition approximation,[12] with a Debye screening length of 9.6 nm. The van der Waals interaction is calculated using Lifshitz theory,[13] resulting in a microsphere−nanoparticle interaction that has an attractive well at contact followed by a weak repulsive barrier comparable to the thermal energy, k_BT, where k_B is Boltzmann's constant and $T = 298$ K indicates the absolute temperature.

All calculations are performed in the canonical (constant *NVT*) ensemble using MC simulations. A cubic simulation box with periodic boundary conditions is used. The large size ratio $\sigma_{\mathrm{micro}}/\sigma_{\mathrm{nano}} \approx 62$ makes the calculations very demanding because the microspheres relax on time scales that are orders of magnitude larger than the relaxation time of the nanoparticles. This problem is overcome by means of the geometric cluster algorithm (GCA),[4,5] which is an MC method that permits the nonlocal, collective displacement of entire groups of particles. As a result of the nonlocal moves, the system evolves according to artificial accelerated dynamics while retaining identical equilibrium properties. In conventional Monte Carlo simulations,[14] nonlocal moves would have an exceedingly small acceptance probability, but the GCA is able to perform cluster moves in a rejection-free manner.

Following the approach of Liu and Luijten,[6] we first investigate the degree of adsorption of nanoparticles on the colloidal surface. These calculations are performed using 10 microspheres at concentration $\phi_{\mathrm{micro}} = 0.10$. A crucial point is that the microsphere−nanoparticle potential $V_{\mathrm{m-n}}$ diverges at contact. Because this would lead to an unphysically strong degree of nanoparticle adsorption (which in reality is prevented by surface roughness), we truncate the potential well at a surface separation D_{cut}, given by the condition $V_{\mathrm{m-n}}(D_{\mathrm{cut}}) = V_{\mathrm{cut}}$. For smaller separations $0 < D < D_{\mathrm{cut}}$, we set the potential equal to a constant value V_{cut}. The resulting potential is depicted in Figure 1 for $V_{\mathrm{cut}} = -7.5k_BT$. The proper value of the cutoff is one of the free parameters in our approach, and we use the observed degree of nanoparticle adsorption as a measure to calibrate V_{cut}. It is important to note that D_{cut} is very small, namely, around 2% of the nanoparticle diameter (i.e., on the order of 4 Å). We investigate three different choices: $V_{\mathrm{cut}}/(k_BT) = -10$, -7.5, and -5.0. For each cutoff, the colloid−nanoparticle pair correlation function exhibits a maximum at contact followed by a minimum at a separation of approximately 5 nm. The number of adsorbed nanoparticles is determined by counting the average number of particles that have a smaller surface separation than the position of this minimum. Figure 2 displays the resulting number of adsorbed nanoparticles per microsphere, $N_{\mathrm{nano}}^{\mathrm{ads}}$, as a function of nanoparticle volume fraction ϕ_{nano}, along with the experimental data.[1] The degree of adsorption increases strongly with increasing magnitude of V_{cut} and at low nanoparticle concentration approaches 100% for $V_{\mathrm{cut}} = -10k_BT$. Upon increasing concentration, the number of adsorbed particles initially increases approximately linearly with ϕ_{nano} but levels off at higher concentrations. A similar plateau was observed in earlier simulations[6] and is due to the electrostatic repulsion between adsorbed nanoparticles. By comparison, the experimental results, which were obtained by measuring the fluorescence intensity of the supernatant solution in systems with labeled polystyrene particles, behave quite irregularly. At low concentrations, virtually 100% adsorption is found, following by a *decrease* in adsorption. At high ϕ_{nano}, the uncertainties become very large. Although it is not possible to determine V_{cut} accurately from this comparison, it appears reasonable to conclude that the optimal value describing the experimental data is bracketed by the parameter values investigated here.

The central property of interest determining whether a colloidal suspension is stable is the *effective* microsphere−microsphere potential, $V_{\mathrm{micro}}^{\mathrm{eff}}$. This potential, which is induced by the nanoparticles, is *independent* of the direct microsphere−microsphere potential,[7,15] so we can omit the electrostatic and van der Waals interactions between the microspheres in the simulations. The total microsphere potential is then simply the sum of these direct interactions and the calculated $V_{\mathrm{micro}}^{\mathrm{eff}}$. The effective interaction can be determined from the microsphere pair correlation function $g(r)$ via $V^{\mathrm{eff}}(r) = -k_BT\ln[g(r)]$, provided that many-body effects are eliminated. This is accomplished by working in the dilute limit, $\phi_{\mathrm{micro}} = 0.01$. At fixed ϕ_{nano}, the

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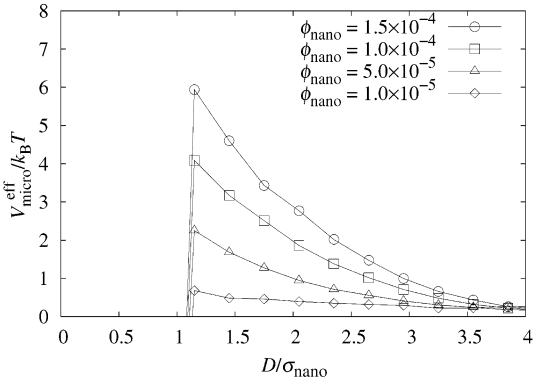

Figure 3. Effective colloid−colloid interaction for different values of $\phi_{\rm nano}$ for $V_{\rm cut} = -10k_{\rm B}T$. The nanoparticles induce an effective barrier with a height that increases with increasing nanoparticle concentration and reaches a value large enough to induce kinetic stabilization at $\phi_{\rm nano} \approx 10^{-4}$. The sharp decrease in the effective potential at $\sigma_{\rm nano}$ is caused by a bridging configuration, where one nanoparticle adsorbs to two microspheres.

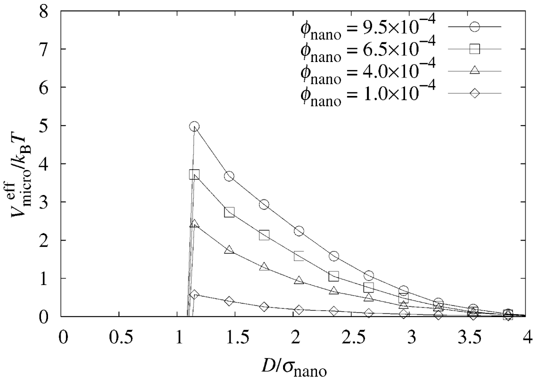

Figure 4. Effective colloid−colloid interaction for different values of $\phi_{\rm nano}$ for $V_{\rm cut} = -7.5k_{\rm B}T$. As in Figure 3 ($V_{\rm cut} = -10k_{\rm B}T$), a repulsive barrier arises with increasing nanoparticle concentration $\phi_{\rm nano}$, but considerably higher concentrations are required. The barrier height becomes sufficient to achieve stabilization for $\phi_{\rm nano} \approx 7 \times 10^{-4}$, which compares favorably to the experimental value $\phi_{\rm nano} \approx 6 \times 10^{-4}$.

computational effort is linearly proportional to the number of microspheres, whereas the number of sampled pair separations increases quadratically. Thus, it is advantageous to use a larger number of microspheres; we use 10 microspheres (rather than the minimum number of 2) in all calculations. The nanoparticle volume fraction is varied from $\phi_{\rm nano} = 1.0 \times 10^{-5}$ to $\phi_{\rm nano} = 6.0 \times 10^{-3}$, which corresponds to a maximum of almost 1.5×10^6 nanoparticles. The GCA is indispensable in these calculations because it is essential to equilibrate both the microspheres and the surrounding distribution of nanoparticles. The pairwise interactions are sufficiently strong to result in quite large energy variations if arbitrary particle displacements are imposed, leading to very small acceptance rates (or very small displacements) in a conventional MC simulation. On the other hand, the pairwise interactions are sufficiently weak to maintain a relatively homogeneous distribution of nanoparticles. Consequently, there is a significant probability of hard-sphere overlaps if a microsphere is displaced, which would again result in a rejected move in a conventional MC approach. The GCA resolves both issues, permitting an efficient exploration of phase space. For each choice of $V_{\rm cut}$ and $\phi_{\rm nano}$, we construct between 3.0×10^6 and 51×10^6 clusters, which corresponds to $(0.33-5.7) \times 10^6$ Monte Carlo sweeps (where a sweep is defined as an update of all large-particle positions). There are between 100 and 4000 nanoparticles in each cluster. Because the GCA guarantees that these are updated at a rate that is controlled by their degree of interaction with the microspheres, their relaxation is very efficient.

Figure 3 displays the effective pair interaction $V^{\rm eff}_{\rm micro}$ as a function of the microsphere separation for different values of $\phi_{\rm nano}$, with $V_{\rm cut} = -10k_{\rm B}T$. At short separations, the potential exhibits a strong attractive minimum, arising from a bridging configuration, in which a single nanoparticle is adsorbed to two microspheres. Closer to contact, the total microsphere interaction (not shown) has an additional minimum owing to the van der Waals attraction between the microspheres. However, if two microspheres approach, then these minima are preceded by a repulsive barrier that rapidly increases in height with increasing $\phi_{\rm nano}$. Note that at the position of this barrier the van der Waals attraction is already negligibly small, so $V^{\rm eff}_{\rm micro}$ in Figure 3 represents the total microsphere interaction. We estimate that kinetic stabilization occurs for a potential barrier of around $4k_{\rm B}T$ to $5k_{\rm B}T$, corresponding to a threshold concentration $\phi^{\rm stable}_{\rm nano}$ of approximately 10^{-4}. (Because the barrier height increases rapidly with increasing $\phi_{\rm nano}$, our result for $\phi^{\rm stable}_{\rm nano}$ does not depend sensitively on the precise criterion for the required barrier height.) This is considerably lower than the experimental result,[1] $\phi^{\rm stable}_{\rm nano} \approx 6 \times 10^{-4}$, which is not surprising because this choice of $V_{\rm cut}$ overestimates the nanoparticle adsorption (cf. Figure 2). Accordingly, we repeat the calculations for $V_{\rm cut} = -7.5k_{\rm B}T$; see Figure 4. The same qualitative behavior is seen, but almost 7 times higher nanoparticle concentrations are required to attain repulsive barriers of the magnitude shown in Figure 3. Specifically, we estimate $\phi^{\rm stable}_{\rm nano} \approx 7 \times 10^{-4}$, in good agreement with the experimental value. As shown in Figure 2, at this threshold concentration only several hundred nanoparticles are adsorbed on each microsphere. Interestingly, if we raise $V_{\rm cut}$ to $-5.0k_{\rm B}T$, we never observe a barrier that is high enough to achieve stabilization; even at $\phi_{\rm nano} = 3.5 \times 10^{-3}$ it reaches a maximum of only $2k_{\rm B}T$.

For a system with an electrostatically induced colloid−nanoparticle attraction, it was found in ref 6 that upon further increase in nanoparticle concentration the effective microsphere potential develops an attractive minimum at a particle separation that exceeds the position of the barrier. To investigate whether this phenomenon also occurs if the weak nanoparticle adsorption is driven by a van der Waals attraction, we perform simulations at values of $\phi_{\rm nano}$ larger than 10^{-3}. Owing to the sheer number of particles, these calculations are computationally very demanding. In addition, the strong repulsion between nanoparticles makes their *effective* volume fraction relatively high, which affects the efficiency of the GCA.[4] Nevertheless, Figure 5 indeed shows the development of a secondary minimum in $V^{\rm eff}_{\rm micro}$ as $\phi_{\rm nano}$ is increased. In accordance with earlier findings,[6,7] the minimum occurs at a microsphere surface separation between 3 and 4 nanoparticle diameters and rapidly becomes deeper at larger $\phi_{\rm nano}$. At $\phi_{\rm nano} = 6.0 \times 10^{-3}$, the attraction is close to $-1k_{\rm B}T$ and we estimate it to exceed $-3k_{\rm B}T$ for concentrations somewhat above 10^{-2}. This attraction will be sufficient to give rise to reentrant gelation, in good agreement with the experimental observations.[1]

We note that the effective colloid−colloid interactions shown in Figures 3−5 are rotationally averaged. The (submonolayer) coverage of nanoparticles will render the microspheres anisotropic. The Monte Carlo simulations do take this anisotropy into account, producing a weighted average over all surface coverages and relative orientations of nanoparticle-covered colloids.

It has been proposed that asymmetric binary mixtures can be understood via an (approximate) mapping onto nonadditive hard-sphere mixtures, which in turn can be analyzed by an exact

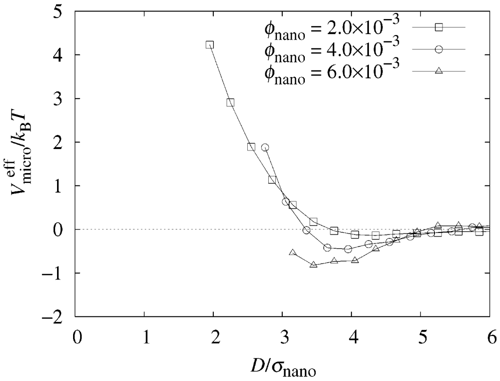

Figure 5. Effective colloid−colloid interaction for nanoparticle interactions $\phi_{\text{nano}} > 10^{-3}$. The same V_{cut} is maintained as in Figure 4. At the higher concentrations shown here, the repulsive barrier persists. (In fact, it is so high that the pair correlation function is vanishingly small for $D \lesssim 3\sigma_{\text{nano}}$, leading to a very low sampling rate in the simulations. This explains the absence of the barrier in the plot for $\phi_{\text{nano}} = 6.0 \times 10^{-3}$.) More important, however, at these concentrations an *attractive minimum* develops for microsphere separations of $3\sigma_{\text{nano}} < D < 4\sigma_{\text{nano}}$. It is estimated that this minimum will reach a value of around $-3k_BT$ for $\phi_{\text{nano}} \approx 10^{-2}$, resulting in gelation.

mapping onto an additive hard-sphere model.[16] Applied to the system studied here, both the repulsion between nanoparticles and the nanoparticle−microsphere attraction lead to a negative nonadditivity. Interestingly, it was found that such negative nonadditivity indeed leads to generalized depletion potentials with features similar to those that we find in the effective potential $V^{\text{eff}}_{\text{micro}}$, namely, a repulsive barrier near contact followed by a second attractive minimum,[16,17] both of which are enhanced compared to an additive hard-sphere mixture.[18]

In summary, we have studied the effective interactions in binary mixtures of silica microspheres and small concentrations of highly charged polystyrene nanoparticles. We have used a model that is sufficiently coarse-grained to permit equilibrium calculations for large-scale systems (up to 1.5×10^6 particles) but that also employs potentials that accurately describe the pairwise interactions, permitting direct comparison with relevant experimental work.[1] In particular, we incorporate the van der Waals attraction between nanoparticles and microspheres, which is responsible for weak adsorption of the nanoparticles. Our findings lead to the following conclusions. (i) Highly charged nanoparticles can kinetically stabilize colloidal microspheres even if the colloid−nanoparticle attraction results from a van der Waals attraction rather than from an induced electrostatic attraction.[6] This confirms experimental observations[1] and corroborates that nanoparticle haloing relies on generic features and hence should be of considerable generality. (ii) The required volume fraction of nanoparticles at the onset of stability can be controlled by tuning the strength of the nanoparticle−microsphere attraction. (iii) Although experimentally the observed number of adsorbed nanoparticles is considered to be negligible,[1] our calculations show that already several hundred nanoparticles per microsphere give rise to an effective microsphere repulsion that is sufficient for kinetic stabilization.

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