Dynamic Colloidal Stabilization by Nanoparticle Halos

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We explore the conditions under which colloids can be stabilized by the addition of smaller particles. The largest repulsive barriers between colloids occur when the added particles repel each other with soft interactions, leading to an accumulation near the colloidal surfaces. At lower densities these layers of mobile particles (nanoparticle halos) result in stabilization, but when too many are added, the interactions become attractive again. We systematically study these effects—accumulation repulsion, reentrant attraction, and bridging—by accurate integral equation techniques.

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Colloidal dispersions—solid particles with radii ranging from a few nm to a few μm, suspended in a liquid solvent—are common in nature and widely used in industry. Blood, paint, ink, and cement are typical examples. Because interatomic dispersion forces induce effective van der Waals interactions with large attractive values at contact, colloids will irreversibly aggregate, which is usually undesirable, unless their surfaces are prevented from approaching too closely. The two most common ways to achieve this are called steric and charge stabilization [1]. Popular strategies for steric stabilization usually involve grafting a layer of polymers onto the colloid surface, resulting in dense repulsive brushes that prevent close contact. For charge stabilization, the route most common in nature, the colloids have surface charges of the same sign, leading to a double layer of microscopic coions and counterions. Adding this effective repulsion to the intrinsic van der Waals attraction results in the famous Derjaguin-Landau-Verwey-Overbeek potential [2], with a metastable free-energy barrier preventing aggregation.

In an important recent development, a third strategy for colloidal stabilization, termed nanoparticle halos, was introduced by Toher and co-workers [3]. By adding charged hydrous zirconia nanoparticles of average radius 3 nm to a suspension of (marginally charged) colloidal silica spheres of radius 285 nm in deionized water, the following behavior was observed: For low nanoparticle number densities the silica spheres aggregate, driven by the intrinsic interaction between two spheres of diameter \( \sigma_{pb} \), induced by smaller spheres. Its properties are determined by the number density \( \rho_s = N_s / V \) of small particles and by the interactions \( \beta \Phi_{bs}(r) \) and \( \beta \Phi_{ss}(r) \); it is independent of the intrinsic interaction \( \beta \Phi_{bb}(r) \) [7]. Introducing small particles that induce a \( \beta V_{bb}^{\text{eff}}(r) \) repulsive enough to counteract an attractive \( \beta \Phi_{bb}(r) \) will stabilize the colloids.

Clearly, a new route to stabilize colloids would have many potential applications. Indeed, nanoparticle halos have already been used to enhance the self-assembly of 3D colloidal crystals on patterned surfaces [5]. Nevertheless, even though this novel stabilization strategy has been demonstrated by experiment, many questions remain about its generic applicability. To address these issues we carry out a systematic theoretical study of the effective interaction \( \beta V_{bb}^{\text{eff}}(r) \) between colloids, induced by (much) smaller particles \( (\beta^{-1} = k_B T) \) is the reduced temperature). We find a large regime of parameter space where \( \beta V_{bb}^{\text{eff}}(r) \) is repulsive enough for stabilization, but this is usually followed by reentrant attraction at a higher small particle packing fraction. The picture that emerges is considerably more subtle than that of a static layer of adsorbed particles akin to steric stabilization. Instead, the nanoparticle halos are dilute, and in dynamic equilibrium with the bulk solution. Moreover, we observe no obvious change in their character when the reentrant attraction kicks in, implying that this phenomenon is more complex than simple depletion attraction.

The key quantity we study is \( \beta V_{bb}^{\text{eff}}(r) \), the effective interaction between two spheres of diameter \( \sigma_{pb} \), induced by smaller spheres. Its properties are determined by the number density \( \rho_s = N_s / V \) of small particles and by the interactions \( \beta \Phi_{bs}(r) \) and \( \beta \Phi_{ss}(r) \); it is independent of the intrinsic interaction \( \beta \Phi_{bb}(r) \) [7]. Introducing small particles that induce a \( \beta V_{bb}^{\text{eff}}(r) \) repulsive enough to counteract an attractive \( \beta \Phi_{bb}(r) \) will stabilize the colloids.

The basic big-small and small-small interactions \( \beta \Phi_{ij}(r) \) are modeled by a hard-core Yukawa form which is versatile without having too many parameters to vary [7]; \( \beta \Phi_{ij}(r) = \infty \) if \( r < \sigma_{ij} \); \( \beta \Phi_{ij}(r) = \phi_{ij}(r) \) for \( r > \sigma_{ij} \), where in each case \( r \) denotes the distance between the centers of the particles, and the Yukawa tail is

\[
\beta \phi_{ij}(r) = \frac{\beta \psi_{ij}}{r} \exp \left[ -\frac{(r - \sigma_{ij})}{\lambda_{ij}} \right],
\]

where \( \sigma_{hs} = \frac{1}{2} (\sigma_{hb} + \sigma_{ss}) \) with \( \sigma_{ss} \) the small particle...
To restrict this vast parameter space somewhat, and inspired by the successful experiments [3], we choose \( \epsilon_{ss} > 0 \) and, initially, \( \epsilon_{bb} = 0 \). The effective potentials \( \beta V_{bb}^{\text{eff}}(r) \) are calculated by using the two-component Ornstein-Zernike (OZ) equations in the \( \rho_b \to 0 \) limit where they decouple, together with the hypernetted chain (HNC) integral equation closure [9], leading to

\[
\beta V_{bb}^{\text{eff}}(r) = -\rho_b \int dr h_{bb}(r)c_{bb}(|r' - r|),
\]

where \( h_{bb}(r) = g_{bb}(r) - 1 \) with \( g_{bb}(r) \) the pair correlation function between big and small particles, and \( c_{bb}(r) \) is the direct correlation function [9]. In this limit, HNC has some important advantages [10] over other popular integral equations such as Percus-Yevick (PY) or Rogers-Young [9]. For example, it is exact for the Asakura-Oosawa (AO) model [4] at all densities \( \rho_b \) (PY is not [10,11]). Moreover, HNC is known to be particularly accurate for soft repulsive potentials of the type we are investigating [9]. To validate our method, we compare, in Fig. 1, the performance of HNC with several simulations [7] for \( \epsilon_{ss} > 0 \) and find excellent agreement. Since we also want to study rather extreme size ratios, we compare, in Fig. 1(b), to depletion potentials for hard spheres (HS) calculated with an accurate density functional theory (DFT) approach [12]. Again HNC performs remarkably well. These results provide the confidence that, even if HNC is not perfectly quantitative, the trends we uncover will be robust, provided we limit ourselves to soft repulsions and low packing fractions [13]. Fortuitously, this appears to be the regime where the nanoparticle halting mechanism operates most effectively.

In order to systematically investigate the conditions for which repulsive stabilization occurs, we calculated, with HNC, \( \beta V_{bb}^{\text{eff}}(r) \) for a large number of parameter combinations. Two typical examples are shown in Fig. 2, demonstrating the common pattern we find: for increasing packing fractions a maximum first appears close to contact and continues to increase until at higher \( \eta_s \), a secondary minimum appears that grows with \( \eta_s \) and rapidly moves to a separation of about one \( \sigma_{ss} \). This sequence of initial stabilization followed by reentrant attraction is similar to that seen in the experiments [3] and is found throughout the parameter regime we investigated.

To further quantify the region of stability, we choose the following measure: For a given set \( \beta \epsilon_{ss}, \lambda_{ss}/\sigma_{ss}, \) and \( q \), we calculate the effective potentials for different \( \eta_s \), as done for Fig. 2. The “stability window” is defined as \( \Delta_\eta = \eta''_s/\eta'_s \), where \( \eta'_s \) is the packing fraction above which the maximum of \( \beta V_{bb}^{\text{eff}}(r) \) is \( > 5 \) (leading to kinetic stabilization), and \( \eta''_s \) is the packing fraction below which the minimum of \( \beta V_{bb}^{\text{eff}}(r) \) is \( < -2 \) (a conservative estimate of where short-range attractions induce aggregation [11]). The way our stability measure \( \Delta_\eta \) varies with potential parameters is depicted in Fig. 3, from which some general trends can be extracted: The size of the window increases with increasing \( \lambda_{ss}/\sigma_{ss} \) and decreasing \( \beta \epsilon_{ss} \) and \( q \). In the HS limit (\( \beta \epsilon_{ss} = 0 \)) we find no window of stability. For a number of points (A–D) in Fig. 3, we show the values of \( \eta''_s \) and \( \eta'_s \). As expected, these packing fractions decrease with increasing \( \beta \epsilon_{ss} \) and \( \lambda_{ss}/\sigma_{ss} \) since the small particles repel each other more and have a larger effective “size.”

The effective repulsion is clearly related to the accumulation of particles near the colloids (nanoparticle halos [3]). We define the “halo” as those particles between \( r = \sigma_{bb} \) and \( r = r_{\text{min}} \), the distance at which the pair correlation function \( g_{bb}(r) \) has its first minimum. The number of particles \( N_{\text{halo}} \), follows from integrating \( g_{bb}(r) \) up to \( r_{\text{min}} \). The 2D packing fraction is given by \( \eta^{\text{2D}} = \frac{1}{4\pi} \rho^{\text{2D}} \sigma_{ss}^2 \), where \( \rho^{\text{2D}} = N_{\text{halo}}/(4\pi \sigma_{bs}^2) \). For all the parameters studied we find the same behavior depicted in the inset of Fig. 3: The halo packing fraction \( \eta^{\text{2D}} \) is linear with \( \eta_s \), and there is no change of slope or other obvious property.
marking either the beginning of stabilization at $\eta^*_i$ or reentrant attraction at $\eta^*_u$. We have also investigated other surface properties such as the adsorption $\Gamma_\beta = - \int h_\beta(r) \, dr$ and the related surface tension $\gamma_s$ [14]. In contrast to polymeric depletants, where $\gamma_s$ helps determine $\beta V_{bb}^{\text{poly}}(r)$ [14], we observe no clear signatures of $\eta^*_i$ or $\eta^*_u$ in the surface tension or the adsorption.

For small $q$ we expect the $g_{\beta s}(r)$ to be similar within corrections $O(q^{-1})$, which explains why the $\eta^2$ vs $\eta_s$ curves are so close for different $q$. However, the stability windows, shown by the symbols in the inset of Fig. 3, differ significantly: They are at lower $\eta_s$ for smaller $q$, something we observe more generally. This can be understood from an approximate Derjaguin [1] argument valid in the small $q$ limit. The potentials scale as $1/q$ times the force between two plates, and so stabilization (and reentrant attraction) is achieved at lower packing fractions. However, this does not easily explain why the window size also grows with decreasing $q$.

The halos are very dilute at stabilization, and we have checked that all layer densities studied are well below that of any two-dimensional freezing transition. In fact, the layers shown in the inset of Fig. 3 are among the densest we investigated; for some $\Phi_{\beta s}$, $\eta_s^{2D}$ can easily be an order of magnitude lower at $\eta^*_u$. At these low packing fractions, the particles rapidly diffuse between halos and the bulk. In contrast to a steric stabilization mechanism, where the layers are static, we emphasize that this nanoparticle halo stabilization mechanism is dynamic.

Further evidence against a naive picture of static layers comes from the reentrant attraction. If the halos would become saturated, so that additional small particles can no longer segregate to the colloidal surface and instead act as depletants, then one might expect a linear dependence of the minimum of $\beta V_{bb}^{\text{poly}}(r)$ on $\eta_s$ as in AO [4] or HS [12] depletion. Instead, the minimum in $\beta V_{bb}(r)$ grows initially as $\eta_s^2$, closely resembling the behavior of the second minimum of HS systems [12], which suggests that it has a similar more complex origin in correlation effects. In fact, both minima would be directly related if the potentials were interpreted in terms of a nonadditive HS reference system with $\sigma_{bb} < \frac{1}{2}(\sigma_{bb} + \sigma_{ss})$, as explained in [15]. The repulsive effective interactions found in many other theoretical studies of $\beta V_{bb}^{\text{poly}}(r)$ can also be qualitatively interpreted in this way (see, e.g., [7] and references therein for a discussion), suggesting that nonadditivity may be fruitfully used to interpret the reentrant attraction [10].

One might argue that since adding an attractive $\phi_{\beta s}(r)$ should increase the number of particles in a layer, this should enhance the stabilization effect. However, we find more subtle scenarios. If we choose $\lambda_{bb} = \lambda_{ss}$, to model residual charge on the large colloids, then for weak attractions the window indeed grows slightly. But, as $\beta \epsilon_{bs}$ becomes more negative, the potentials rapidly develop a large attractive component. This phenomenon, sometimes called bridging for polymeric additives [1], results from configurations where the two bigger additives are both attracted to the same set of smaller particles [10]. An example of bridging is demonstrated in Fig. 4(a) and is representative of what we find more generally: the stability window $\Delta \eta$ initially grows slightly, but then rapidly disappears, typically around $\beta \epsilon_{bs} \lesssim -1.5$.

On the other hand, a dramatic enhancement of the stabilization occurs for longer ranged colloid-nanoparticle attractions, as demonstrated in Fig. 4 for $\lambda_{bb} = 3 \lambda_{ss}$. The bridging effect is bypassed and the first minimum shifts up to positive absolute values; in fact, for these parameters we find no reentrant attraction within the range where we trust HNC [13]. In general, we find this effect for $\lambda_{bb} > \lambda_{ss}$, but exactly where it kicks in depends on $q$ and the other potential parameters. In all cases studied, the 2D layer densities are still very low so that the halos are dilute; typically for more negative $\beta \epsilon_{bs}$ bridging sets in.

![FIG. 3](color online) The “equi-$\Delta \eta$” lines denote different values of the stability window $\Delta \eta = \eta^*_u - \eta^*_s$ for size ratios $q = 0.01$ and $q = 0.05$. For points A–D the stability window packing fractions, for $q = 0.01$, are listed in the format ($\eta^*_u$, $\eta^*_s$). Inset: the 2D packing fraction $\eta_s^{2D}$ of a halo for different size ratios $q$. The potential parameters are $\beta \epsilon_{bs} = 2$ and $\lambda_{ss}/\sigma_{ss} = 0.5$. The symbols denote $\eta^*_u$ and $\eta^*_s$ for $q = 0.01$ (circles), $q = 0.05$ (diamonds), and $q = 0.1$ (squares).

![FIG. 4](color online) (a) Adding an attractive $\phi_{bs}(r)$ generates a deep minimum due to bridging effects when $\lambda_{bb} = \lambda_{ss}$. (b) A dramatic stabilization effect occurs for weak longer ranged attractions: $\lambda_{bb} = 3 \lambda_{ss} = 3 \sigma_{ss}$, and $\beta \epsilon_{bs} = -0.5$. 

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again [10]. Of course when $\beta \phi_{bs}(r)$ is attractive enough to induce static saturated layers, then the particles would be sterically stabilized. But technically this is a nonequilibrium effect: it works only if the colloidal particles are first isolated from each other on the time scale that the (saturated) layer forms.

Finally, having systematically explored the effect of different parameters on $\beta V_{bs}^{el}(r)$, we make some recommendations for experiments. For $\varepsilon_{bs} = 0$ the best stabilization should occur for modestly charged small additives (nanoparticles) since the stability windows are largest for small $q$, modest $\beta \varepsilon_{ss}$, and large $\lambda_{ss}/\sigma_{ss}$. Small $\sigma_{ss}$ are needed to enhance the latter parameter, since the (Debye) screening length is typically fixed by solution conditions, e.g., $\lambda_{ss} = 30$ nm for 0.1 mM monovalent salt concentration. Another argument in favor of small particles concerns the dynamic nature of the layers. If the big particles are driven at velocities such that the smaller particles can no longer adiabatically follow, then the stabilization effect may disappear. Since the self-diffusion coefficients of the nanoparticles scale as $1/\sigma_{ss}^2$ [1], this again favors small particles. Moreover, larger windows $\Delta \eta$ also enhance stability under halo fluctuations.

Whereas adding charge to the colloids can destroy the stabilization effect, a modest but longer ranged attraction $\beta \phi_{bs}(r)$ can significantly enhance it. The latter effect could be induced by residual van der Waals attractions, although this recommendation must be tempered by the difficulty of adding van der Waals attractions between similar species without simultaneously significantly increasing them between similar species. On the other hand, the advantage of small van der Waals attractions (which are independent of debye screening length), is that the ratio $\lambda_{bs}/\lambda_{ss}$ can be tuned by changing salt concentration. This adds another handle for engineering effective potentials and concomitant phase behavior [10].

We observe the same general trends seen in the experiments of Ref. [3], such as lower $\eta_i^*$ with smaller $q$ and values of $\eta_i^{2D}$ well below saturation. A direct quantitative comparison, however, is hampered by their use of polydispersible small particles, and the difficulty in deriving accurate potentials $\beta \phi_{ij}(r)$. Taking their estimates ($\beta \varepsilon_{ss} = 6$, $\lambda_{ss}/\sigma_{ss} = 0.6$) we find a smaller window $\Delta \eta = 2$, at higher $\eta_i^*$ than what they observed. The difference could stem from a small attractive $\beta \phi_{bs}(r)$ or from polydispersity (preliminary calculations suggest that this lowers the effective $\eta_i^*$ and $\eta_i^{2D}$ [16]).

In conclusion, we discovered a substantial parameter regime where the addition of small (nano) particles can stabilize bigger colloids. Fortuitously, this occurs where the flexible HNC integral equation is most reliable. We usually find a stability window of packing fractions, above or below which the colloids aggregate again. The effects are significantly enhanced for weak longer ranged attractive $\beta \phi_{bs}(r)$. Although the stabilization is clearly related to the formation of diffusive accumulation layers around the bigger particles, we find no simple relationship to layer properties. This suggests these effects are related to more complex correlations. Colloidal stabilization by dynamic nanoparticle halos should be widely applicable and complimentary to existing steric and charge stabilization techniques [1,2]. This new mechanism may also be relevant for smaller scale biological interactions [17].

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Note added.—Upon completion of this work we became aware of a study by Liu and Luijten [18] which uses different techniques but arrives at similar conclusions.

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10. S. Karanikas and A. A. Louis (to be published).
13. No claim is being made for the general accuracy of HNC for all parameter values. For example, the predictions for HS begin to show important quantitative deviations for $\eta_i^* > 0.3$ and the comparison with simulations of Ref. [7] is less accurate for attractions ($\varepsilon_{ss} < 0$).
16. P. Bryk (private communication).