Generalized effective depletion potentials

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We propose that the behavior of asymmetric binary fluid mixtures with a large class of attractive or repulsive interparticle interactions can be understood by mapping onto effective non-additive hard-sphere models. The latter are best analyzed in terms of their underlying depletion potentials which can be exactly scaled onto known additive ones. By tuning the non-additivity, a wide variety of attractive or repulsive generalized depletion potential shapes and associated phase behavior can be “engineered”, leading, for example, to two ways to stabilize colloidal suspensions by adding smaller particles.

Colloidal suspensions are complex mixtures of mesoscopic solute particles and smaller solvent particles. Examples include a wide variety of organic or inorganic solutes, ranging from proteins to micelles to polymeric composites to ceramic materials etc., suspended in polar or non-polar solvents. Varying the interactions between the constituent particles results in a broad range of equilibrium and non-equilibrium fluid behavior. This tunability has led to the wide spread industrial and biological applications of colloidal suspensions. Some more recent developments include the design of complex self-assembled materials such as photonic band-gap crystals by use of templates, and new experimental advances that allow colloidal interactions to be directly measured with a greatly increased accuracy.

In all the applications mentioned above, the design of a colloidal fluids with certain desired properties requires control over the inter particle interactions. These interactions are typically effective, that is to say they are a combination of direct interactions (such as Coulomb forces) with indirect interactions mediated through the solvent and the other solute particles. One of the best known is the indirect depletion interaction, where one set of (typically smaller solute or solvent) particles induces an interaction between another set of particles. Depletion potentials were first calculated for mixtures of polymers and colloids and, with the advent of new experimental and theoretical techniques, they have been the subject of intense recent interest.

Theoretical work has often focussed on the binary hard-sphere (HS) model, for which a depletion induced phase separation for size-ratios’ \( q = \sigma_{ss}/\sigma_{bb} < 0.2 \) was suggested (\( \sigma_{ss} \) is the diameter of the big \((b)\) or small \((s)\) particles). A key advance was made by Dijkstra et al., who used an effective one-component depletion potential picture to show that the fluid-fluid phase-separation found with a two-component integral equation technique by Biben and Hansen was metastable w.r.t. a fluid-solid phase-transition. More generally, their approach added to the growing consensus that a carefully derived effective potential is a powerful tool for analyzing the behavior of an asymmetric binary mixture, at least for size-ratios \( q \leq 0.3 \) where many-body interactions are not thought to be important (see e.g. for some recent reviews). The key step in all these approaches is integrating out the smaller component of a binary mixture to leave a new one-component system with an effective interaction between the big particles.

Most theories of depletion have considered only hardcore interactions leading to purely entropic depletion potentials. Their range varies with \( \sigma_{ss} \) while increasing the small particle density \( \rho_s \) or packing fraction \( \eta_s = \pi \rho_s \sigma_s^3/6 \) increases the depth of the (always) attractive well at contact, and possibly adds enhanced oscillations at larger separations \( r \).

There have been a number of recent attempts to go beyond purely entropic depletion by including extra interactions between the particles of a binary HS mixture. Of course many different kinds of extra interactions can be added, leading to a seemingly enormous increase in complexity. However, in this letter we propose that the effect of a wide variety of these extra interactions on depletion potentials can be understood by a simple mapping onto a non-additive HS mixture model, for which the depletion potentials can be calculated by a second exact mapping or scaling onto those of an additive system.

Since the phase behavior of many binary fluids can be well understood on the basis of these depletion potentials, this implies that our (double) mapping can be used to analyze a wide variety of interacting asymmetric binary mixtures. These ideas can also be turned around, leading to the possibility of explicitly engineering a wide variety of \textit{generalized depletion potential} shapes, including potentials that are repulsive at contact, by not only varying the usual parameters \( \rho_s \) and \( q \), but also by tuning the interparticle interactions to vary the non-additivity.

Non-additive binary HS models are defined by specifying the cross-diameter.
\[ \sigma_{bs} = \frac{1}{2} (\sigma_{ss} + \sigma_{bb}) (1 + \Delta). \]  

When \( \Delta = 0 \), the model follows the Lorentz mixing rule, and is traditionally called additive (not to be confused with pairwise additivity of potentials), that is the cross-diameter is simply the sum of the two radii, exactly what one would expect on purely geometric grounds. If \( \Delta > 0 \) or \( \Delta < 0 \) the system shows positive or negative non-additivity respectively. As shown in Fig. 1, each big particle excludes a volume \( v_h = \pi \sigma_{bb}^3/6 \) from the centers of the smaller particles. When the depletion layers of the two big particles (width defined as \( h = \sigma_{bs} - \sigma_{bb}/2 = \frac{1}{2} (\sigma_{ss} + \Delta (\sigma_{ss} + \sigma_{bb})) \)) begin to overlap, then the small particles can gain free volume \( v_\Delta \), leading to a depletion interaction.

\[ \beta V_{eff}(r) = -\rho_s \frac{\pi}{4} \left( \sigma_{bb}(2h)^2 + 2 \frac{2}{3}(2h)^3 \right). \]  

For a fixed number density \( \rho_s \), non-additivity can be introduced in two ways:

**Case (A)** Fix the depletion layer width \( h \), (or equivalently \( \sigma_{bs} \)), and vary \( \Delta \) by changing the small particle diameter \( \sigma_{ss} \). The effect on depletion pair-potentials \( \beta V_{eff}(r) \) is shown in Fig. 2. For increasing positive non-additivity the correlation induced maximum decreases and the potential tends towards the (ideal) Asakura-Oosawa (AO) limit; the contact value remains relatively constant, as was found earlier. In contrast, for increasing negative non-additivity the contact value increases markedly, leading to the possibility of strongly repulsive interactions. A naive application of the simplest depletion picture where \( \beta V_{eff}(r = \sigma_{bb}) = -\Pi_s v_\Delta \) gives the opposite effect, since decreasing \( \Delta \) by increasing \( \sigma_{ss} \) increases the packing fraction \( \eta_s = \pi \rho_s \sigma_{ss}^3/6 \) and therefore the small particle osmotic pressure \( \Pi_s \), while keeping \( v_\Delta \) unchanged, seemingly leading to a more attractive effective potential. However, a more careful analysis reveals that increasing \( \eta_s \) leads to well-developed solvation shells around a single big particle. When two big particles approach, the overlap of the solvation shells leads to the repulsive interactions, as well as larger oscillations in the pair potentials. We found that the amplitude of this repulsion becomes larger for smaller size-ratios, with values possible of many times \( k_B T \).

**Case (B)** Fix the small-particle hard-core diameter \( \sigma_{ss} \), and vary \( \Delta \) by changing \( h \) (or equivalently \( \sigma_{bs} \)). The dominant effect on depletion pair-potentials is to shift them along \( r \) as shown in Fig. 2. In this case both positive and negative non-additivity change the well-depth at contact significantly because changing \( h \) changes the amount of volume doubly excluded when two big particles approach. This can be illustrated at the simple AO level where the potential at contact is given by

\[ \beta V_{AO}(r = \sigma_{bb}) = -\rho_s \frac{\pi}{4} \left( \sigma_{bb}(2h)^2 + 2 \frac{2}{3}(2h)^3 \right). \]  

On the other hand, the correlation induced maximum remains roughly the same since \( \eta_s \) is constant, leading to similar solvation layers of the small particles around a big particle.
The included simulation data for $\beta \epsilon$ of Case (B) change according to Case (A), i.e. varying $b$ but keeping $\sigma_{ss}$ constant. Here $q = 0.2$, $\eta_s = 0.2$ and line-styles denote the same $\Delta s$ as in Fig. 3. Inset: Depletion potentials when $\beta V_{bs}(r) = \epsilon \exp[-\kappa (r - \sigma_{bs})]/r$ is added to a binary HS mixture are compared to the non-additive HS case with $\Delta$ calculated by our simple mapping. Here $\eta_s = 0.116$, $q = 0.2$, $\kappa \sigma_{ss} = 4$ is fixed and $\beta \epsilon$ is varied. The included simulation data for $\beta \epsilon = -0.32$ [14] helps confirm the accuracy of our new direct DFT approach.

The depletion potentials for (i) ($\Delta < 0$) and (ii) ($\Delta > 0$) change according to case (A), which is depicted in Fig. 2, while the depletion potentials for (iii) ($\Delta > 0$) and (iv) ($\Delta < 0$) change according to case (B), as depicted in Fig. 3. This picture agrees qualitatively with calculations of other authors of depletion potentials for non-HS systems. Examples of the pathways above include: (i) Fig. 4 of [13]; (ii) Fig. 8 of [13], Fig. 4 of [1]; (iii) Fig. 5 of [14]; Fig. 3 of [13]; (see also [23] for a recent experimental and [24] for a recent theoretical mapping of this type of interaction onto an AO potential). (iv) Fig. 4 of [13]; Fig. 4 of [14], Fig. 7 of [14] and Fig. 4 of [1].

Keep in mind, however, that these calculations were done with a number of approximate techniques which may not always give quantitatively reliable results, especially for contact values [1]. Even so, our mapping scheme to non-additivity clearly qualitatively rationalizes the dominant changes in depletion potentials caused by changing a variety of inter-particle interactions.

It would be interesting to make this qualitative correspondence more quantitative. We were able to extend the quantitatively reliable DFT method described in [13] to systems with an arbitrary $V_{bs}(r)$ potential (details will be published elsewhere). In the inset of Fig 3 we compare these to non-additive HS potentials with $\Delta$ determined by our aforementioned mapping procedure. This gives a reasonably good representation of the well depth, but does slightly less well for the repulsive barrier. With our very simple mapping procedure, we expect that the quantitative agreement will deteriorate for very strongly attractive $V_{bs}(r)$ or $V_{ss}(r)$, but the qualitative picture should remain the same.

From the above it is clear that non-additivity has a profound effect on depletion potentials, implying that this should also be reflected in phase-behavior. For more symmetric mixtures the effect of interparticle interactions on phase-stability has traditionally been understood in terms of conformal-solution theory [20]. For asymmetric mixtures, our depletion potentials help generalize these ideas. For example, Vliegenthart and Lekkerkerker [23] have recently shown that the fluid-fluid critical point of many one-component fluids occurs when the reduced second virial-coefficient $B_2/B_2^{HS} \approx -1.5$. We checked that this works well for the depletion potential simulations of Dijkstra et al. [10, 11], suggesting that this surprisingly accurate criterion can also be used to predict the effect of non-additivity on fluid-fluid phase-separation. In Fig 4 we plot the effect of the $\eta_s$ on the second virial coefficients calculated from depletion potentials. Firstly, for the additive case we find that $B_2/B_2^{HS} < -1.5$ only for size-ratios $q \lesssim 0.11$ (For $q = 0.1$ there might be an upper critical point!). But even without attributing quantitative accuracy to the Vliegenthart Lekkerkerker criterion, the upper limit of $q$ that allows fluid-fluid phase-separation is clearly bounded by $0.1 \leq q \leq 0.2$, since $B_2/B_2^{HS}$ remains positive for any $\eta_s$ if $q > 0.2$, while it goes well below $-1.5$ for $q < 0.1$. This finding helps in understanding earlier results obtained with (approximate) 2-component integral equation studies [8] as well as some direct simulations [22], lending support to our argument that the underlying depletion potentials from which the $B_2$ are derived are a key to understanding the full phase-behavior of the asymmetric two-component systems.

Next we turn to the effect of non-additivity on the fluid-fluid phase-separation. Fig. 4 shows that for $q = 0.1$ a very small non-additivity, of the order of a 5% change in $\sigma_{ss}$, or a 0.5% change in $\sigma_{bb}$, is enough to dramatically change the behavior of $B_2/B_2^{HS}$. For other size-ratios we find similar effects. For example if $\Delta = q/20$ we find that (metastable) fluid-fluid phase-separation can occur for size-ratios up to $q = 0.4$, while if $\Delta = -q/20$, it will only occur for size-ratios $q \lesssim 0.05$. Clearly, even a very small negative non-additivity strongly suppresses phase-separation, while positive non-additivity strongly enhances it. This is consistent with and helps rationalize some earlier 2-component studies [26, 28].

Binary mixtures may also undergo fluid-solid phase-
separation which, for example, is the thermodynamically stable phase-transition in additive HS mixtures [10]. Recently, one of us [23] has shown that for short range potentials the fluid-solid transition shifts to low values of \( \eta_b = \pi \rho_b \sigma_{bb}^3 / 6 \) when the potential well-depth at contact is near \( \beta V_{eff} (r = \sigma_{bb}) \approx -2.5 \); this effect is largely independent of other details such as the range or oscillations of the potential. This suggests that introducing any non-additivity according to case (B) will strongly affect the fluid-solid behavior. Similarly adding negative non-additivity according to case (A) will suppress fluid-solid phase-separation, but positive non-additivity will not change the fluid-solid phase-boundaries much, which is confirmed by comparing the additive (\( \Delta = 0 \)) HS to pure AO (\( q = \Delta \)) simulations of Dijkstra et al. [17].

\[ B_2 / B_2^{HS} \] plotted v.s. the packing fraction of the small particles \( \eta_s \). Fluid-fluid phase-separation is expected when \( B_2 / B_2^{HS} < -1.5 \) [23] (horizontal line).

The stabilization of colloidal suspensions is critical to many industrial and experimental applications [1]. The arguments above for both fluid-fluid and fluid-solid phase-separation suggest that the addition of smaller particles may provide such a stabilization mechanism against demixing for colloidal suspensions as long as \( \Delta < 0 \). This can be achieved by pathway (i), adding a repulsive \( V_{ss}(r) \), or by pathway (iv), adding an attractive \( V_{bs}(r) \).

In conclusion then, we combined a new approximate and a new exact mapping to show that the non-additive HS mixture model provides an intuitive and general organizing framework within which to understand the effective depletion potentials induced by a large class of interactions \( V_{bs}(r) \) or \( V_{ss}(r) \). These generalized depletion potentials can be crafted into many different shapes, and provide access to the phase-behavior of interacting asymmetric binary mixtures. Clearly much more can be done by both theories and experiments to exploit the flexibility of these potentials and to “engineer” desired phase-behavior in colloidal suspensions. We hope this letter has shown some promising new directions in which to embark.

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