Generalized depletion potentials

LETTER TO THE EDITOR

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Abstract
We propose that the behaviour 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
analysed 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 behaviour can be 'engineered', leading, for example, to two ways to
stabilize colloidal suspensions by adding smaller particles.

Varying the interactions between the mesoscopic constituent particles in colloidal dispersions—examples include proteins, micelles, polymeric composites, ceramic materials etc in polar or non-polar solvents—results in a broad range of equilibrium and non-equilibrium fluid behaviour. It is this tunability which has led to the widespread industrial and biological applications of colloidal suspensions [1]. Some very promising recent experimental advances allow for an exquisite control over the colloidal interactions, leading, for example, to the design of complex self-assembled materials such as photonic band-gap crystals by use of templates [2]. Concurrently, new measurement techniques are being developed that directly determine these interactions with a greatly increased accuracy [3].

Designing colloidal fluids with certain desired properties requires direct control over the interparticle interactions. These interactions are typically effective, i.e. they are a combination of direct interactions (such as Coulomb forces) with indirect interactions mediated through the solvent and the other solute particles [4–6]. One of the best known is the indirect depletion interaction, where one set of (typically smaller solute or solvent) particles induces an effective interaction between another set of particles. Depletion potentials were first calculated for mixtures of polymers and colloids [7] and, with the advent of new experimental and theoretical techniques, they have been the subject of intensive recent interest [8–12, 14]. In this letter we show how a generalization of the depletion potential concept leads to new ways to tune and understand the properties of asymmetric binary colloid mixtures.

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Theoretical work has often focused 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 [8] (here $\sigma_{\alpha\alpha}$ is the diameter of the big (subscript b) or small (subscript s) particles). An important advance was made by Dijkstra *et al* [10], 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 [8] was metastable w.r.t. a fluid–solid phase transition. More generally, their approach added to the growing consensus that a carefully derived effective pair potential is a powerful tool for analysing the behaviour of an asymmetric binary mixture, at least for size ratios $q \leqslant 0.3$ where many-body interactions are not thought to be important (see e.g. [4–6] 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 hard-core interactions leading to purely entropic depletion potentials. Their range varies with σ_{ss}, while increasing the small-particle density ρ_s or packing fraction $\eta_s = \pi \rho_s \sigma_{ss}^3/6$ increases the depth of the (always) attractive well at contact, and possibly adds enhanced oscillations at larger separations r [7, 9, 14].

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 [15–19]. Of course many different kinds of extra interaction 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, which are well understood [14].

The phase behaviour of many asymmetric binary fluids (with independent components) can be understood on the basis of these depletion potentials [4–6, 10, 11], which then implies that our (double) mapping can be used to analyse a wide variety of interacting asymmetric binary mixtures[4]. These ideas can also be turned around, leading to the possibility of explicitly engineering a wide variety of *generalized depletion potential* shapes, including potentials that are repulsive at contact by tuning the interparticle interactions to vary the non-additivity.

Non-additive binary HS models are defined by specifying the cross-diameter [21]

$$\sigma_{bs} = \frac{1}{2}(\sigma_{ss} + \sigma_{bb})(1 + \Delta). \tag{1}$$

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 figure 1, each big particle excludes a volume $v_b = \pi \sigma_{bs}^3/6$ from the centres of the smaller particles. When the depletion layers of the two big particles (width defined as $l = \sigma_{bs} - \sigma_{bb}/2 = \frac{1}{2}(\sigma_{ss} + \Delta(\sigma_{ss} + \sigma_{bb}))$) begin to overlap, then the small particles can gain free volume v_Δ, leading to a depletion interaction.

To calculate these potentials we first note that the depletion potential $\beta V_{eff}(r)$ depends only on the big–small and small–small interactions ($\beta V_{bs}(r)$ and $\beta V_{ss}(r)$ respectively), but not on any direct big–big interaction $\beta V_{bb}(r)$, which can simply be added to the depletion potential [6, 14]. For non-additive systems at fixed ρ_s this means that the depletion potential is determined by σ_{bs} and σ_{ss}, and is equivalent to an additive one with the same parameters!

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[4] We restrict ourselves here to mesoscopic binary colloidal mixtures where the so-called volume terms do not contribute to the phase behaviour [10]. If one were instead to integrate out the *microscopic* co- and counter-ions, this might lead to volume terms which affect phase behaviour.
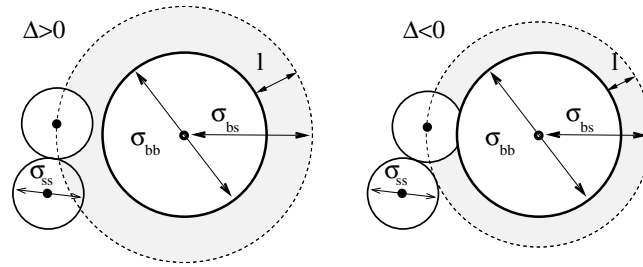
Figure 1. Centres of the small particles of diameter σ_{ss} are excluded from the shaded depletion layer of width l around each big particle of diameter σ_{bb}. If $l < \frac{1}{2}\sigma_{ss}$ then $\Delta < 0$ (negative non-additivity). If $l > \frac{1}{2}\sigma_{ss}$, then $\Delta > 0$ (positive non-additivity).

Only the cut-off due to σ_{bb} is different. For example, if one has an expression for the additive potential in terms of ρ_b, q and the scaled distance $p = r/\sigma_{bb}$, then a potential with $\Delta \neq 0$ is given by

$$\beta V_{eff}(\rho_s, q, \Delta, p) = \beta V_{eff}(\rho_s, q', \Delta = 0, (q'/q)p)$$

where $q' = \sigma_{ss}/(2\sigma_{bs} - \sigma_{ss}/2)$. Details of this (perhaps surprising) exact mapping by scaling to additive potentials will be given elsewhere [22]. The depletion potentials for additive systems can be calculated to quantitative accuracy by a density functional theory (DFT) technique [14], and we checked that the scaling procedure above exactly reproduces recent direct DFT calculations of non-additive depletion potentials [20].

For a fixed number density ρ_s, non-additivity can be introduced in two ways:

- **Case (A).** Fix the depletion layer width l (or equivalently σ_{bs}), and vary Δ by changing the small-particle diameter σ_{ss}. The effect on depletion pair potentials $\beta V_{eff}(r)$ is shown in figure 2. For increasing positive non-additivity the correlation-induced maximum decreases and the potential tends towards the (ideal) Asakura–Oosawa (AO) [7] limit; the contact value remains relatively constant, as was found earlier [20]. In contrast,
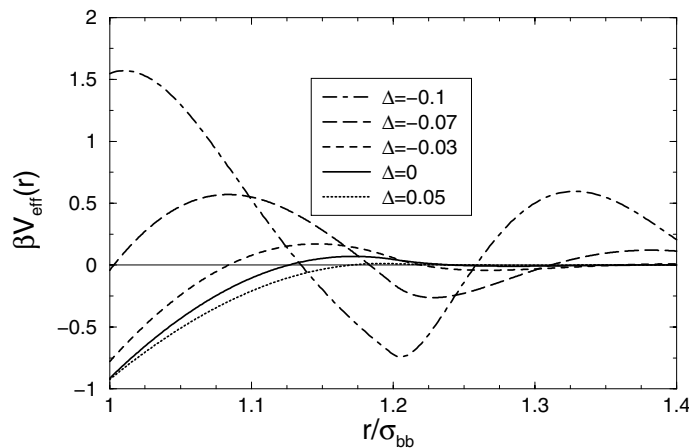

Figure 2. Depletion potentials when parameters are changed according to **case (A)**, i.e. varying σ_{ss} but keeping l constant. Here $q = 0.2$, and $4\pi\rho_s l^3/3 = 0.1$. The potentials are calculated by an exact scaling from known additive DFT results [14].

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 $\beta V_{eff}(r = \sigma_{bb}) = -\Pi_s v_\Delta$ would give the opposite effect, since decreasing Δ by increasing σ_{ss} increases the packing fraction $\eta_s = \pi \rho_s \sigma_{ss}^3 / 6$ and therefore the small-particle osmotic pressure Π_s, while keeping v_Δ unchanged, seemingly leading to a more attractive effective potential. However, a more careful analysis reveals that increasing η_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 σ_{ss}, and vary Δ by changing l (or equivalently σ_{bs}). The dominant effect on depletion pair potentials is to shift them along r as shown in figure 3. In this case both positive and negative non-additivity change the well depth at contact significantly because changing l changes the amount of volume doubly excluded when two big particles approach. This can be understood even at the simple AO level where the potential at contact is given by [6]

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

On the other hand, the correlation-induced maximum remains roughly the same since η_s is constant, leading to similar solvation layers of the small particles around a big particle.
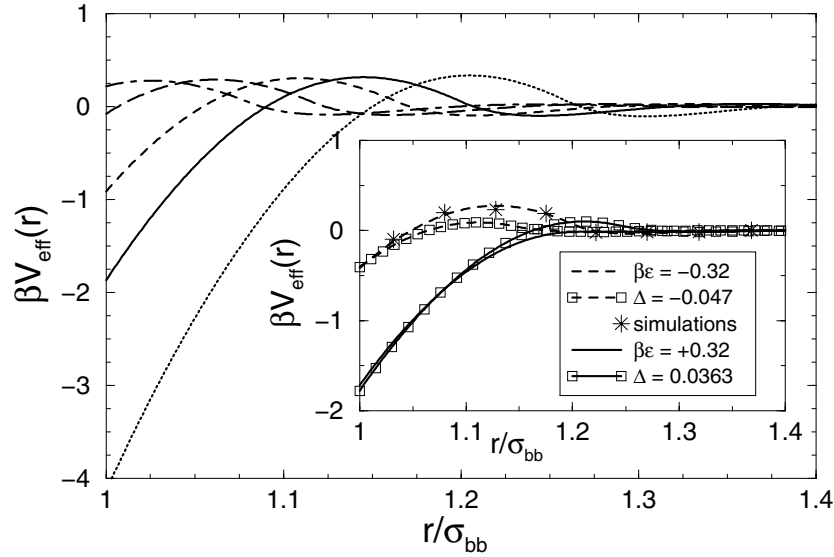

Figure 3. Depletion potentials when parameters are changed according to **case (B)**, i.e. varying l but keeping σ_{ss} constant. Here $q = 0.2$, $\eta_s = 0.2$ and line styles denote the same Δ-values as in figure 2. Inset: depletion potentials when $\beta V_{bs}(r) = \epsilon \exp[-\kappa(r - \sigma_{bs})]/r$ is added to a binary HS mixture are compared to the non-additive HS case with Δ 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 simulation data for $\beta\epsilon = -0.32$ included [17] help confirm the accuracy of our new direct DFT approach.

With the insight gained from analysing non-additive depletion potentials, we next pose the question: what happens to $\beta V_{eff}(r)$ for a given binary HS mixture when more general attractive

or repulsive interactions $\beta V_{ss}(r)$ or $V_{bs}(r)$ are added? Inspired by some well-established ideas from the theory of simple liquids [21], we map onto effective HS diameters as follows:

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^0 + \int (\exp[-\beta V_{\alpha\beta}(r)] - 1) \, dr$$

which is a procedure similar to the well-known Barker–Henderson approach [23]. Here $\sigma_{\alpha\beta}^0$ denotes the original effective HS diameters without the extra interaction. In this way the additional interactions can be mapped onto an effective non-additive HS model as follows:

  (i) repulsive $\beta V_{ss}(r)$: $\sigma_{bs} = \sigma_{bs}^0$; $\sigma_{ss} > \sigma_{ss}^0$; $\Delta < 0$;
 (ii) attractive $\beta V_{ss}(r)$: $\sigma_{bs} = \sigma_{bs}^0$; $\sigma_{ss} < \sigma_{ss}^0$; $\Delta > 0$;
(iii) repulsive $\beta V_{bs}(r)$: $\sigma_{bs} > \sigma_{bs}^0$; $\sigma_{ss} = \sigma_{ss}^0$; $\Delta > 0$;
(iv) attractive $\beta V_{bs}(r)$: $\sigma_{bs} < \sigma_{bs}^0$; $\sigma_{ss} = \sigma_{ss}^0$; $\Delta < 0$.

The depletion potentials for **(i)** ($\Delta < 0$) and **(ii)** ($\Delta > 0$) change according to **case (A)**, which is depicted in figure 2, while the depletion potentials for **(iii)** ($\Delta > 0$) and **(iv)** ($\Delta < 0$) change according to **case (B)**, as depicted in figure 3. This picture agrees qualitatively with calculations of other authors of depletion potentials for non-HS systems. Examples of the pathways above include: **(i)** figure 4 of [19]; **(ii)** figure 8 of [16], figure 4 of [4]; **(iii)** figure 5 of [15]; figure 3 of [16] (see also [24] for a recent experimental and [25] for a recent theoretical mapping of this type of interaction onto an AO potential); **(iv)** figure 4 of [16], figure 4 of [17], figure 7 of [18], and figure 4 of [4]. 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 [6][5]. Even so, with the possible exception of case **(ii)** our scheme of mapping to non-additivity *qualitatively* rationalizes the dominant changes in depletion potentials caused by changing a variety of interparticle interactions.

It would be interesting to make this qualitative correspondence more quantitative. We were able to extend the quantitatively reliable DFT method described in [14] to systems with an arbitrary potential $V_{bs}(r)$ (details will be published elsewhere). In the inset of figure 3 we compare these to non-additive HS potentials with Δ determined by our aforementioned mapping procedure. This gives a 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[6].

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 behaviour. For more symmetric mixtures the effect of interparticle interactions on phase stability has traditionally been understood in terms of conformal-solution theory [21]. Our depletion potential arguments help generalize these ideas to very asymmetric mixtures, as will be illustrated below. For example, Vliegenthart and Lekkerkerker [26] have recently shown that the fluid–fluid phase transition in many one-component fluids occurs when the reduced second virial coefficient $B_2/B_2^{HS} < -1.5$. 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 figure 4 we plot the effect of η_s on the second virial coefficients calculated from depletion potentials. For the additive case we find that $B_2/B_2^{HS} < -1.5$ only for size ratios $q < 0.11$ (for $q = 0.1$ there might be an

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[5] Recent simulations [13] have shown that case **(ii)** is especially hard to model theoretically, with results which do not always fit into our mapping scheme. This is being actively explored at present.
[6] Again, recent simulations [13] show that the mapping is no longer quantitative for large interactions, especially when they are attractive (cases **(ii)** and **(iv)**).
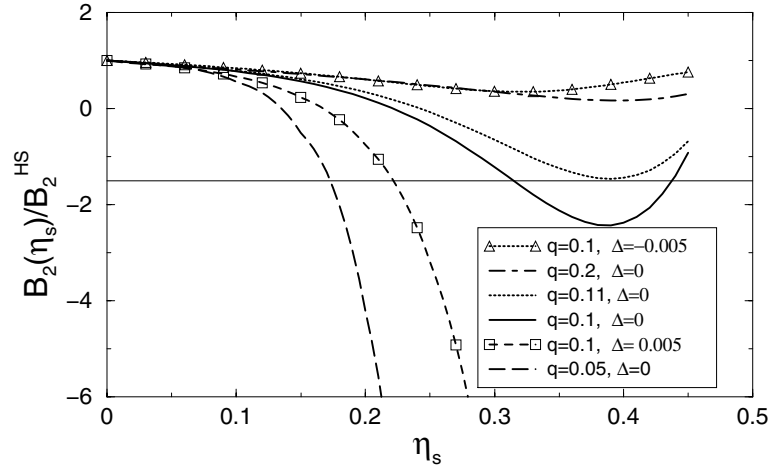
Figure 4. Reduced second virial coefficient of the big particles, B_2/B_2^{HS}, plotted versus the packing fraction of the small particles, η_s. Fluid–fluid phase separation is expected when $B_2/B_2^{HS} < -1.5$ [26] (horizontal line).

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 $0.1 \leqslant q \leqslant 0.2$, since B_2/B_2^{HS} remains positive for any η_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) two-component integral equation studies [8] as well as some direct simulations [12], lending support to our argument that the underlying depletion potentials from which the values of B_2 are derived are a key to understanding the full phase behaviour of the asymmetric two-component systems.

Next we turn to the effect of non-additivity on the fluid–fluid phase separation. Figure 4 shows that for $q = 0.1$ a very small non-additivity, of the order of a 5% change in σ_{ss} or a 0.5% change in σ_{bs}, is enough to dramatically change the behaviour 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 $q < 0.05$. 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 two-component studies [27–29].

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 [6,29] 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 behaviour. 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, a prediction that is confirmed by comparing the additive ($\Delta = 0$) HS to pure AO ($q = \Delta$) simulations of Dijkstra *et al* [10, 11].

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 behaviour 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 behaviour in colloidal suspensions. We hope that this letter has shown some promising new directions in which to embark.

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