Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Material

Effective buoyancy. We provide here a formal derivation of the buoyancy force F_1 acting onto a test type-1 colloid immersed in a solution of type-2 particles, expressed in purely thermodynamic terms. The density profile of a suspension of particles in the presence of a gravitational field is described by the hydrostatic equilibrium condition

$$\frac{d\Pi[n_2(z),T]}{dz} = -m_2 g\, n_2(z), \tag{S1}$$

where m_2 is the buoyant mass of type-2 particles, Π the osmotic pressure, and we assume that the number density n_2 may depend on z. The gravitational length $\ell_g = k_B T/(m_2 g)$ defines the characteristic scale of the spatial modulations of the density profile: here and in the following we assume that ℓ_g is the largest length in the problem, a condition easily met in colloidal suspensions. Under this assumption, the contribution to the buoyancy force acting onto a test particle (denoted by index 1) inserted in this solution, due to the presence of type-2 particles, is given by Eq. (1) in the text:

$$F_1(z) = -m_2\, g\, n_2(z) \int d\mathbf{r}\, h_{12}(r), \tag{S2}$$

where $h_{12}(r) = g_{12}(r) - 1$. This expression depends on the mutual correlations between the two species but can be equivalently written in terms of purely thermodynamic quantities. Regarding the system as a binary mixture where component 1 is extremely diluted, the Ornstein-Zernike relation in the $n_1 \to 0$ limit (see Ref. [14])

$$h_{12}(r) = c_{12}(r) + n_2 \int d\mathbf{x} c_{12}(\mathbf{r}-\mathbf{x})\, h_{22}(\mathbf{x}) \tag{S3}$$

allows to express the integral of $h_{12}(r)$ in terms of the integral of the direct correlation function $c_{12}(r)$ and the long wave-length limit of the structure factor of a type-2 one component fluid $S_{22}(0)$:

$$\int d\mathbf{r}\, h_{12}(r) = S_{22}(0) \int d\mathbf{r}\, c_{12}(r). \tag{S4}$$

Both terms at right hand side can be expressed as thermodynamic derivatives of the Helmholtz free energy of the mixture A via the compressibility sum rules (Ref. [17]):

$$\begin{aligned} n_2\, S(0) =& k_B T \left[\frac{\partial^2 (A/V)}{\partial n_2^2} \right]^{-1} \\ k_B T \int d\mathbf{r}\, c_{12}(r) =& - \frac{\partial^2 (A/V)}{\partial n_1\, \partial n_2}. \end{aligned} \tag{S5}$$

According to the McMillan-Mayer theory of solutions, the contribution of the solvent to the total free energy can be disregarded if effective interactions among particles are introduced. In the limit $n_1 \to 0$ we can express the free energy derivatives appearing in Eq. (S5) in terms of the osmotic pressure:

$$\Pi = -\frac{A}{V} + n_2 \frac{\partial (A/V)}{\partial n_2} + n_1 \frac{\partial (A/V)}{\partial n_1} \tag{S6}$$

leading to

$$\begin{aligned} F_1 =& \frac{\partial^2 (A/V)}{\partial n_1 \partial n_2} \left[\frac{\partial^2 (A/V)}{\partial n_2^2} \right]^{-1} m_2 g \\ =& \left[\frac{\partial \Pi}{\partial n_1} - k_B T \right] \left[\frac{\partial \Pi}{\partial n_2} \right]^{-1} m_2 g \end{aligned} \tag{S7}$$

which coincides with Eq. (2) in the paper. This shows that the contribution to the buoyancy force on a type-1 particle due to the presence of component 2 is proportional to the buoyant mass m_2. It is interesting to investigate the limiting form of the buoyancy force when the type-1 particle is just a "tagged" type-2 particle, with identical physical properties. In this case the system is effectively one-component and then $\frac{\partial \Pi}{\partial n_1} = \frac{\partial \Pi}{\partial n_2}$. The buoyancy force acting onto a particle in the solution acquires the form:

$$F = mg \left[1 - k_B T \left(\frac{\partial \Pi}{\partial n} \right)^{-1} \right]. \tag{S8}$$

It is instructive to deduce Eq. (S8) with a different approach, which highlights its physical meaning. The equilibrium sedimentation profile of a suspension of interacting Brownian particles is usually derived by balancing gravity with the diffusive term deriving from gradients in the osmotic pressure. However, fixing the attention on a single test particle, we can try to summarize the effect of all the other particles as an "effective field" F adding to the bare gravitational force $-mg$. From the Smoluchowski equation, the combination of these two contributions yield a density profile:

$$k_B T \frac{dn}{dz} = n(F - mg),$$

that, combined with the hydrostatic equilibrium equation (S1), yields for F the expression in Eq. (S8). Hence, the equilibrium sedimentation profile of an interacting suspension can be equivalently viewed in terms of the probability distribution for the position of a test particle subjected to a spatially–varying gravitational field, whose dependence on z is dictated by the equation of state of the suspension.

In hard sphere systems we can easily obtain an approximate expression for the buoyancy force from Eq. (S7): a rough estimate of the excluded volume effects in the osmotic pressure can be obtained following the familiar Van der Waals argument:

$$\begin{aligned} \Pi(n_1, n_2) - n_1 k_B T &= \frac{N_2\, k_B T}{V - N_1 \frac{4}{3}\pi (R_1 + R_2)^3} \\ &\sim n_2 k_B T \left[1 + n_1 \frac{4}{3}\pi (R_1 + R_2)^3 \right] \end{aligned} \tag{S9}$$

By substituting this form into Eq. (S7) we recover the simple result, already quoted in a slightly different form in the main paper

$$F_1 = m_2 g\, \Phi_2 \left(1 + \frac{1}{q}\right)^3 \tag{S10}$$

A more careful evaluation is obtained by starting from the analytical expression of the excess free energy of a binary hard sphere mixtures provided by Mansoori *et al.* (J. Chem. Phys. **54**, 1523, 1971). The result can be conveniently expressed in terms of the *effective mass density of the surrounding medium* ρ^* defined by

$$F_1 = \frac{4}{3}\pi\, R_1^3 \rho^* g \tag{S11}$$

The explicit expression for the effective density reads:

$$\frac{\rho^*}{m_2 n_2} = \Big[6 + (1-q)^2(2+q)\,(1-\Phi_2)^3 - 3(1-q^2)(1-\Phi_2)^2 - 2\,\left[(1-q)^2(2+q) - q^3\right]\,(1-\Phi_2)\Big]\,\left[(1-\Phi_2)^4 + \Phi_2(8-2\Phi_2)\right]^{-1}$$

The dependence of ρ^* on the size and volume fraction of type-2 particles is shown in Fig. 1. For $q > 1$, i.e. when a small test particle is immersed into a suspension of big particles, the buoyancy force displays a pronounced maximum. In the $q \to \infty$ limit, the maximum buoyancy force is attained at $\Phi_2 \sim 0.154$, where it reduces to a sizeable fraction of the effective weight of a type-2 particle: $F_1 \sim 0.055\, m_2 g$.

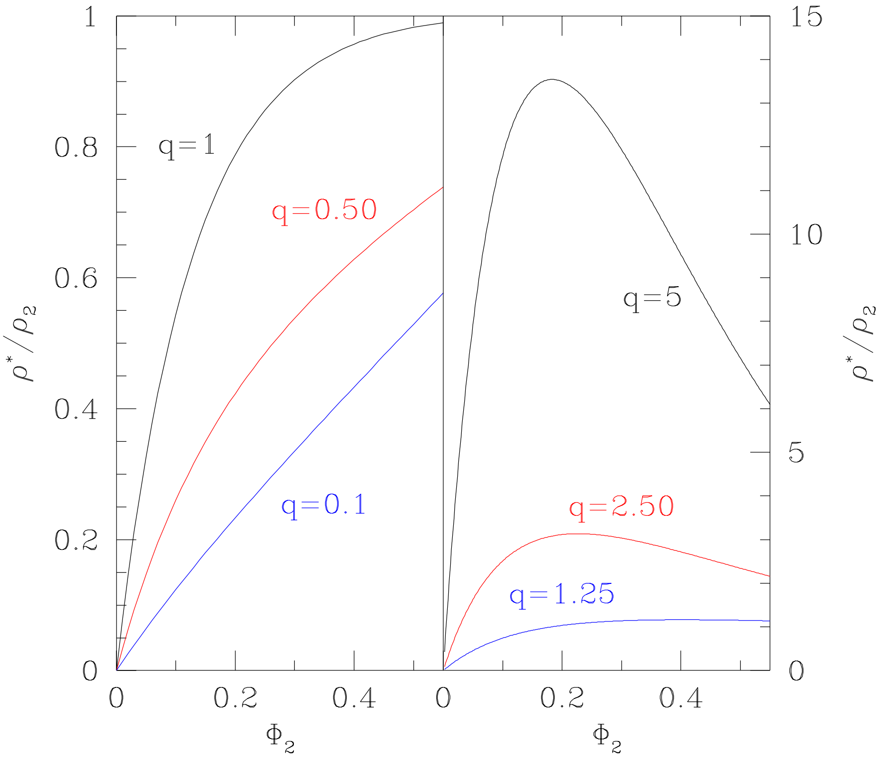

Figure 1: Effective mass density of the surrounding medium, relative to the type-2 mass density as a function of Φ_2 for different $q = R_2/R_1$. Left panel: results for $q \leq 1$. Right panel: $q > 1$. Note the change of scale in the vertical axis.

Distribution of guest particles at equilibrium. The hydrostatic equilibrium condition for a suspension of type-1 particles reads:

$$\frac{d\Pi}{dz} = n_1\,[-m_1\,g + F_1] \tag{S12}$$

where Π, n_1 and m_1 are the osmotic pressure, average local density and buoyant mass respectively. In the limit of short range interspecies correlations, the excess buoyant force F_1 due to the presence of type-2 particles is given by Eq. (S10), while in the diluted limit of type-1 particles the ideal gas equation of state $\Pi_1 = n_1 k_B T$ holds. Substituting these results in Eq. (S12) we find:

$$k_B T\,\frac{dn_1}{dz} = n_1\,g\left[-m_1 + m_2\,\Phi_2(z)\left(1+\frac{1}{q}\right)^3\right] \tag{S13}$$

which defines the number density profile of type-1 particles. The maximum of the resulting distribution corresponds to the vanishing of the right hand side of this expression, given by condition (3) of the main paper:

$$\Phi_2^* \equiv \Phi_2(z^*) = \frac{\Phi_2^{iso}}{(1+q)^3} \tag{S14}$$

where $\Phi_2^{iso} = (m_1/m_2)q^3$ coincides with the isopycnic volume fraction defined in the main paper. By expanding $\Phi_2(z)$ around the position of this maximum z^*, Eq. (S13) becomes:

$$\begin{aligned}\frac{dn_1}{dz} =& n_1\,\frac{m_2\,g}{k_B T}\,\frac{d\Phi_2(z)}{dz}\Big|_{z=z^*}\left(1+\frac{1}{q}\right)^3 (z-z^*)\\ =& n_1\,\frac{d\Phi_2(z)}{dz}\Big|_{z=z^*}\,\frac{(z-z^*)}{\ell_{g1}\,\Phi_2^*}\end{aligned} \tag{S14}$$

whose solution $n_1(z)$ is a gaussian centered in $z = z^*$ with standard deviation given by Eq. (5) of the main paper.