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

$$\frac{d\Pi[n_2(z), T]}{dz} = -m_2 g n_2(z),$$  \hspace{1cm} (S1)

where $m_2$ is the buoyant mass of type-2 particles, $\Pi$ 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 $\ell_g$ 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:

$$F_1(z) = -m_2 g n_2(z) \int dr h_{12}(r),$$  \hspace{1cm} (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])

$$h_{12}(r) = c_{12}(r) + n_2 \int dxc_{12}(r - x) h_{22}(x)$$  \hspace{1cm} (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 $S_{22}(0)$:

$$\int dr \ h_{12}(r) = S_{22}(0) \int dr \ c_{12}(r). \quad (S4)$$

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]):

$$n_2 S(0) = k_B T \left[ \frac{\partial^2 (A/V)}{\partial n_2^2} \right]^{-1}$$

$$k_B T \int dr \ c_{12}(r) = -\frac{\partial^2 (A/V)}{\partial n_1 \partial n_2}. \quad (S5)$$

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:

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

leading to

$$F_1 = \frac{\partial^2 (A/V)}{\partial n_1 \partial n_2} \left[ \frac{\partial^2 (A/V)}{\partial n_2^2} \right]^{-1} m_2 g$$

$$= \left[ \frac{\partial \Pi}{\partial n_1} - k_B T \left[ \frac{\partial \Pi}{\partial n_2} \right] \right]^{-1} m_2 g \quad (S7)$$

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:

$$F = m g \left[ 1 - k_B T \left( \frac{\partial \Pi}{\partial n} \right)^{-1} \right]. \quad (S8)$$
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:

\[
\Pi(n_1, n_2) - n_1 k_B T = \frac{N_2 k_B T}{V - N_1 \frac{4}{3} \pi (R_1 + R_2)^3}
\]

\[
\sim n_2 k_B T \left[ 1 + n_1 \frac{4}{3} \pi (R_1 + R_2)^3 \right]
\]

(S9)

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

\[
F_1 = m_2 g \Phi_2 \left( 1 + \frac{1}{q} \right)^3
\]

(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 \(\rho^*\) defined by

\[
F_1 = \frac{4}{3} \pi R_1^3 \rho^* g
\]

(S11)
The explicit expression for the effective density reads:

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

The dependence of $\rho^*$ 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 $\Phi_2$ 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:

\[
\frac{d\Pi}{dz} = n_1 \left[ -m_1 g + F_1 \right]
\]  
(S12)

where \(\Pi, n_1\) 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:

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

\[
\Phi_2^* \equiv \Phi_2(z^*) = \frac{\Phi_2^{iso}}{(1 + q)^3}
\]  
(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:

\[
\frac{dn_1}{dz} = n_1 \frac{m_2 g}{k_B T} \frac{d\Phi_2(z)}{dz} \left|_{z=z^*} \left( 1 + \frac{1}{q} \right)^3 (z - z^*) \right.
\]

\[
= n_1 \frac{d\Phi_2(z)}{dz} \left|_{z=z^*} \frac{(z - z^*)}{\ell g_1 \Phi_2^*} \right.
\]  
(S14)

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