# Supporting Information

## Sedimentation dynamics and equilibrium profiles in multicomponent mixtures of colloidal particles

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# 1 Force balances in suspensions of particles

## 1.1 Suspension with one type of particle

The concentration-dependent part of thermodynamic force on a particle in a one-component suspension of monodisperse particles at constant temperature, omitting the labels for constant temperature for clarity, can be written as

$$F_i^{\mathrm{th}} = -\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P \frac{\partial \phi}{\partial z} \tag{1}$$

where the label c is used to denote the colloidal particles, the label F is used to denote the suspending fluid and $\phi$ is the volume fraction of colloidal particles. The derivative of the chemical potential to particle concentration can be rewritten using the method of Jacobian determinants [1, 2]

$$\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P = \left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_{\mu_{\mathrm{F}}} + \frac{(\partial \mu_{\mathrm{c}}/\partial P)_{n_{\mathrm{c}}}\,(\partial \mu_{\mathrm{F}}/\partial \phi)_P}{(\partial \mu_{\mathrm{F}}/\partial P)_{n_{\mathrm{c}}}}\ . \tag{2}$$

The derivative $(\partial \mu_{\mathrm{c}}/\partial P)_{n_{\mathrm{c}}}$ is the specific volumes of the colloidal particles, which for an incompressible suspension is equal to the particle volume $v_{\mathrm{c}}$. The derivative $(\partial \mu_{\mathrm{F}}/\partial P)_{n_{\mathrm{c}}}$ can be shown to be [2]

$$\left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi}\right)_{n_{\mathrm{c}}} = \bar{v_{\mathrm{F}}} - \phi\,\kappa \left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi}\right)_P \tag{3}$$

where $\kappa = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility. For an incompressible suspension ($\kappa = 0$), the above expression simplifies to the molecular volume of the fluid $v_{\mathrm{F}}$.

Using the Gibbs-Duhem equation for this suspension at constant (local) pressure [3, 4]:

$$0 = n_{\mathrm{F}}\,\mathrm{d}\mu_{\mathrm{F}} + n_{\mathrm{c}}\,\mathrm{d}\mu_{\mathrm{c}} \qquad\qquad \mathrm{d}\mu_{\mathrm{F}} = -\frac{n_{\mathrm{c}}}{n_{\mathrm{F}}}\,\mathrm{d}\mu_{\mathrm{c}}\ , \tag{4}$$

we can rewrite Equation 2 for an incompressible suspension:

$$\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P = \left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_{\mu_{\mathrm{F}}} + \frac{v_{\mathrm{c}} n_{\mathrm{c}}}{v_{\mathrm{F}} n_{\mathrm{F}}}\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P = \left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_{\mu_{\mathrm{F}}} + \frac{\phi}{1-\phi}\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P \tag{5a}$$

$$\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_P = (1-\phi)\left(\frac{\partial \mu_{\mathrm{c}}}{\partial \phi}\right)_{\mu_{\mathrm{F}}} = \frac{v_{\mathrm{c}}(1-\phi)}{\phi}\left(\frac{\partial \Pi}{\partial \phi}\right)_{\mu_{\mathrm{F}}}\ . \tag{5b}$$

We note that the differential equation describing the SDE in a one-component suspension can also be obtained by considering the forces acting on the fluid. The gravitational force:

$$F_{\mathrm{F}}^{\mathrm{grav}} = -v_{\mathrm{F}}\rho_{\mathrm{F}} g - v_{\mathrm{F}}\,\frac{\partial P^{\mathrm{h}}}{\partial z} = -v_i(\rho_{\mathrm{F}} - \rho_{\mathrm{susp}})g \tag{6}$$

should be balanced by the thermodynamic force [4]:

$$F_{\mathrm{F}}^{\mathrm{th}} = -\left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi}\right)_P \frac{\partial \phi}{\partial z} = +v_{\mathrm{F}} \left(\frac{\partial \Pi}{\partial \phi}\right)_{\mu_{\mathrm{F}}} \frac{\partial \phi}{\partial z} \tag{7}$$

which, after rewriting, leads to:

$$F_{\mathrm{F}}^{\mathrm{grav}} + F_{\mathrm{F}}^{\mathrm{th}} = 0 \tag{8a}$$

$$\frac{\partial \phi}{\partial z} = \frac{(\rho_{\mathrm{F}} - \rho_{\mathrm{susp}})g}{(\partial \Pi / \partial \phi)_{\mu_{\mathrm{F}}}} = -\frac{\phi(\rho_{\mathrm{c}} - \rho_{\mathrm{F}})g}{(\partial \Pi / \partial \phi)_{\mu_{\mathrm{F}}}} \tag{8b}$$

### 1.2 Suspension with multiple types of particles

In general, in a multicomponent suspension of particles, the thermodynamic force depends on the concentration gradient of all components:

$$F_i^{\mathrm{th}} = -\frac{\mu_i}{\partial z} = -\sum_j \left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{P,n_k} \frac{\partial \phi_j}{\partial z} \tag{9}$$

where $n_k$ indicates that the derivative is taken at a constant concentration of all other components $k \neq j$. For $i = j$, and assuming that the suspension is incompressible, we have:

$$\left(\frac{\partial \mu_i}{\partial \phi_i}\right)_{P,n_k} = \left(\frac{\partial \mu_i}{\partial \phi_i}\right)_{\mu_{\mathrm{F}},n_k} + \frac{(\partial \mu_i/\partial P)_{n_i,n_k}\,(\partial \mu_{\mathrm{F}}/\partial \phi_i)_{P,n_k}}{(\partial \mu_{\mathrm{F}}/\partial P)_{n_i,n_k}} \tag{10a}$$

$$= \left(\frac{\partial \mu_i}{\partial \phi_i}\right)_{\mu_{\mathrm{F}},n_k} + \frac{v_i}{v_{\mathrm{F}}} \left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi_i}\right)_{P,n_k} . \tag{10b}$$

For $i \neq j$, we have:

$$\left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{P,n_k} = \left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{\mu_{\mathrm{F}},n_k} + \frac{(\partial \mu_i/\partial P)_{n_j,n_k}\,(\partial \mu_{\mathrm{F}}/\partial \phi_j)_{P,n_k}}{(\partial \mu_{\mathrm{F}}/\partial P)_{n_j,n_k}} \tag{11a}$$

$$= \left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{\mu_{\mathrm{F}},n_k} + \frac{v_i}{v_{\mathrm{F}}} \left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi_j}\right)_{P,n_k} . \tag{11b}$$

Summation yields:

$$F_i^{\mathrm{th}} = -\sum_j \left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{\mu_{\mathrm{F}},n_k} \frac{\partial \phi_j}{\partial z} - \frac{v_i}{v_{\mathrm{F}}} \sum_j \left(\frac{\partial \mu_{\mathrm{F}}}{\partial \phi_j}\right)_{P,n_k} \frac{\partial \phi_j}{\partial z} \tag{12a}$$

$$= -\sum_j \left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{\mu_{\mathrm{F}},n_k} \frac{\partial \phi_j}{\partial z} + v_i \frac{\partial \Pi}{\partial z} \tag{12b}$$

where we used $v_{\mathrm{F}}\,\mathrm{d}\Pi = -\mathrm{d}\mu_{\mathrm{F}}$ [1, 4]. This final equation is in agreement with the thermodynamic force we used in our generalized theory in the main text.

## 2 Osmotic pressure gradient in equilibrium

First of all, we note that the Gibbs-Duhem (GD) equation for the system with the fluid treated as a continuum,

$$\mathrm{d}\Pi = \sum_i n_i \,\mathrm{d}\mu_i , \tag{13}$$

where the sum runs over all particle types (solvent excluded), allows writing the gradient of the chemical potential as a gradient of the osmotic pressure, for the case of incompressible particles and an incompressible fluid. For a single-component suspension, we obtain

$$v_{\mathrm{c}} \frac{\partial \Pi}{\partial \phi} = \phi \frac{\partial \mu_{\mathrm{c}}}{\partial \phi} . \tag{14}$$

We note that the GD equation (Equation 13) follows logically from the definitions of the osmotic pressure and the chemical potential:

$$\mu_i = v_i \frac{\partial f}{\partial \phi_i} \tag{15a}$$

$$\Pi = \phi \sum_i \phi_i \frac{\partial}{\partial \phi_i}\left(\frac{f}{\phi}\right) \tag{15b}$$

where $\phi = \sum_i \phi_i$ is the total particle volume fraction and $f$ is the free energy density of the mixture.

If we now multiply the equation for the total force (cf. Equation 3.6 in the main text):
by $n_i$, sum over all particle species, and insert the GD equation 13 for the gradients of the chemical potential, and Equation 1.1 from the main text for the suspension density, we arrive at the following expression for the osmotic pressure gradient in equilibrium:

$$\frac{\partial \Pi}{\partial z} = -g(\rho_{\text{susp}} - \rho_{\text{F}})\ . \tag{16}$$

# 3 Power series expansion of BMCSL equation of state

The excess chemical potential of an ion in the BMCSL equation of state can be written as

$$\begin{aligned} \frac{\mu_i^{\text{ex}}}{k_{\text{B}}T} &= -\left(1 + \frac{2{\xi_2}^3{\sigma_i}^3}{\phi^3} - \frac{3{\xi_2}^2{\sigma_i}^2}{\phi^2}\right)\ln(1-\phi) + \frac{3\xi_2\sigma_i + 3\xi_1{\sigma_i}^2 + \xi_0{\sigma_i}^3}{1-\phi} \\ &\quad + \frac{3{\xi_2}^2{\sigma_i}^2}{\phi(1-\phi)^2} + \frac{3\xi_1\xi_2{\sigma_i}^3}{(1-\phi)^2} - {\xi_2}^3{\sigma_i}^3\frac{\phi^2 - 5\phi + 2}{\phi^2(1-\phi)^3} \end{aligned} \tag{17}$$

where $\xi_k$ $(k = 0, 1, 2)$ is given by $\xi_k = \sum_j \phi_j {\sigma_j}^{k-3}$ where $j$ runs over all particles. We rewrite the products $\xi_k {\sigma_i}^{3-k}$ as follows

$$\xi_k {\sigma_i}^{3-k} = \sum_j \phi_j {\sigma_i}^{3-k} {\sigma_j}^{k-3} = \phi \sum_j {\alpha_{ij}}^{3-k}\,\zeta_j \tag{18}$$

where $\alpha_{ij} = \sigma_i/\sigma_j$ is the ratio of the particle sizes and $\zeta_j = \phi_j/\phi = \phi_j/\sum_m \phi_m$ is the relative volume fraction of particles $j$ (e.g., in a mixture of 50 particles of type 1 and 50 particles of type 2 that have a three times smaller volume than particles 1, $\zeta_1 = 0.75$ and $\zeta_2 = 0.25$). Consequently, $\sum_j \zeta_j = 1$. We assume that the weighted sums of the fractions of particles ($\sum_j \alpha_{ij}^k\,\zeta_j$) are independent of the overall volume fraction $\phi$ and we abbreviate $\sum_j \alpha_{ij}\,\zeta_j = A$, $\sum_j \alpha_{ij}^2\,\zeta_j = B$ and $\sum_j \alpha_{ij}^3\,\zeta_j = C$.

In order to find an expansion of Equation 17 we rewrite it in terms of $A$, $B$ and $C$

$$\frac{\mu_i^{\text{ex}}}{k_{\text{B}}T} = -\left(1 + 2A^3 - 3A^2\right)\ln(1-\phi) + \frac{3A + 3B + C}{1/\phi - 1} + \frac{3A^2\phi + 3AB\phi^2}{(1-\phi)^2} - A^3\,\frac{\phi^3 - 5\phi^2 + 2\phi}{(1-\phi)^3}\ . \tag{19}$$

The power series expansion around $\phi = 0$ of Equation 19 reads

$$\begin{aligned} \lim_{\phi\to 0}\frac{\mu_i^{\text{ex}}}{k_{\text{B}}T} &= \sum_{\lambda=1}^{\infty}\frac{1}{\lambda}\left(1 + 2A^3 - 3A^2\right)\phi^\lambda + (3A + 3B + C)\phi^\lambda + 3A^2\lambda\phi^\lambda + 3AB(\lambda-1)\phi^\lambda + (\lambda^2 - 2\lambda - 1)A^3\phi^\lambda \\ &= \sum_{\lambda=1}^{\infty}\left[\left(\lambda^2 - 2\lambda - 1 + \frac{2}{\lambda}\right)A^3 + 3\left(\lambda - \frac{1}{\lambda}\right)A^2 + 3(\lambda-1)AB + 3A + 3B + C + \frac{1}{\lambda}\right]\phi^\lambda \end{aligned} \tag{20}$$

Several useful limits of this power series are considered in detail.

### 3.1 Equally sized spheres

In the limit of equally sized spheres, $\alpha_{ij} = 1$ for all $i$ and $j$. Consequently, $A = 1$, $B = 1$ and $C = 1$ and

$$\lim_{\phi\to 0} \frac{\mu_i^{\mathrm{ex,CS}}}{k_{\mathrm{B}}T} = \sum_{\lambda=1}^{\infty} \left[\lambda^2 + 4\lambda + 3\right] \phi^{\lambda} \tag{21}$$

which yields the prefactors of the power series expansion of the Carnahan-Starling equation of state for hard spheres (8, 15, 24, 35, 48, ...).

### 3.2 Infinitely small particles $i$, $\sigma_1 \ll \sigma_2$

In the limit of infinitely small particles $i$, $\alpha_{ii} = 1$ and $\alpha_{ij} = 0$ for $i \neq j$, and $\zeta_i = 0$. Consequently, $A = 0$, $B = 0$ and $C = 0$, and

$$\lim_{\phi\to 0} \frac{\mu_i^{\mathrm{ex,Bik}}}{k_{\mathrm{B}}T} = \sum_{\lambda=1}^{\infty} \frac{1}{\lambda} \phi^{\lambda} \tag{22}$$

which yields the prefactors of the Bikerman expression (1, 1/2, 1/3, 1/4, ...).

### 3.3 Tracer limit $\phi_1 \ll \phi_2$

In the tracer limit with $\phi_1 \ll \phi_2$, $\zeta_1 = 0$ and $\zeta_2 = 1$. Consequently, $A = \alpha_{12} = \sigma_1/\sigma_2$, $B = \alpha_{12}^2$ and $C = \alpha_{12}^3$, and

$$\lim_{\phi\to 0} \frac{\mu_i^{\mathrm{ex,trace}}}{k_{\mathrm{B}}T} = \sum_{\lambda=1}^{\infty} \frac{1}{\lambda} \left[(1+\lambda\alpha)^3 + 3(\lambda-1)\alpha^2 + (\lambda-1)(\lambda-2)\alpha^3\right] \phi_2^{\lambda} \tag{23}$$

where we abbreviated $\alpha = \alpha_{12}$. Note that this equation will hold for all tracer particles that have a negligible concentration, in multicomponent mixtures with one majority species (type 2 in the above example).

Note that in the above three limits (Sections 1.1, 1.2 and 1.3), the assumption that the weighted sums of the fractions of particles are independent of the overall volume fraction $\phi$ is no longer needed, since the particles either have the same volume (Section 1.1), one has a negligible volume (Section 1.2) or one has a negligible volume fraction (Section 1.3). Therefore, these limits can safely be applied in sedimentation problems. The full expression in Equation 19 can be used in homogenized mixtures. In sedimentation problems, where the local fraction of one component does depend on the overall volume fraction, the power series expansion in Equation 19 must be applied with care.

# 4 BMCSL equation of state for connected spheres (dimers, trimers and colloidal chains)

For the free energy density of the BMCSL equation of state of mixtures of monomers, dimers, trimers, etc., we propose:

$$\frac{f}{k_{\mathrm{B}}T} = \sum_i \frac{\phi_i}{N_i v_i} \ln\frac{\phi_i}{v_i} + \frac{6}{\pi}\left[-\xi_{0,N}\ln(1-\phi) + \frac{3\xi_1\xi_2}{1-\phi} + \frac{{\xi_2}^3}{\phi(1-\phi)^2} + \frac{{\xi_2}^3\ln(1-\phi)}{\phi^2}\right] \tag{24}$$

where

$$\xi_{0,\,N} = \sum_j \phi_j \sigma_j^{-3} N_j^{-1} \,. \tag{25}$$

Using Equation 15a, we obtain the following expression for the excess chemical potential *per bead* (which is the hard sphere subelement of the dimers, trimers, etc.) in a BMCSL mixture of (clusters of) hard spheres:

$$\begin{aligned}\frac{\mu_{i,\,N}^{\mathrm{ex}}}{k_{\mathrm{B}}T} \quad &= \quad -\left(\frac{1}{N_i} + \frac{2{\xi_2}^3{\sigma_i}^3}{\phi^3} - \frac{3{\xi_2}^2{\sigma_i}^2}{\phi^2}\right)\ln(1-\phi) + \frac{3\xi_2\sigma_i + 3\xi_1{\sigma_i}^2 + \xi_{0,\,N}{\sigma_i}^3}{1-\phi} \\ &\quad + \frac{3{\xi_2}^2{\sigma_i}^2}{\phi(1-\phi)^2} + \frac{3\xi_1\xi_2{\sigma_i}^3}{(1-\phi)^2} - {\xi_2}^3{\sigma_i}^3\frac{\phi^2-5\phi+2}{\phi^2(1-\phi)^3}\end{aligned} \tag{26}$$

and the ideal part of the chemical potential *per bead* is

$$\mu_{i,\,N}^{\mathrm{id}} = \frac{k_\mathrm{B}T}{N_i}\ \ln\phi_i\ . \tag{27}$$

An elegant expansion of excess chemical potential term in Equation 26 can be found, following the same strategy as outlined in the previous section. We use

$$\xi_{0,\,N}{\sigma_i}^3 = \phi\sum_j N_j^{-1}{\alpha_{ij}}^3\,\zeta_j = \phi C_N \qquad \text{and} \qquad \frac{\partial\xi_{0,\,N}}{\partial\phi_i} = \frac{\xi_{0,\,N}}{N_i{\sigma_i}^3} \tag{28}$$

The resulting expansion in powers of $\phi$ can then be written as

$$\begin{aligned}\lim_{\phi\to 0}\frac{\mu_i^{\mathrm{ex}}}{k_\mathrm{B}T} &= \sum_{\lambda=1}^{\infty}\frac{1}{\lambda}\left(\frac{1}{N_i}+2A^3-3A^2\right)\phi^\lambda\ +(3A+3B+C_N)\phi^\lambda \\ &\quad +3A^2\lambda\phi^\lambda\ +3AB(\lambda-1)\phi^\lambda\ +(\lambda^2-2\lambda-1)A^3\phi^\lambda \\ &= \sum_{\lambda=1}^{\infty}\left[\left(\lambda^2-2\lambda-1+\frac{2}{\lambda}\right)A^3+3\left(\lambda-\frac{1}{\lambda}\right)A^2+3\left(\lambda-1\right)AB+3A+3B+C_N+\frac{1}{\lambda N_i}\right]\phi^\lambda\ .\end{aligned} \tag{29}$$

# 5 Direct differential equations of sedimentation profiles in two- and three-component mixtures

The general differential equation that describes the sedimentation profiles in multicomponent mixtures of colloidal particles is given by Equation 4.1 in the main text. For each component, the differential equation depends on all gradients $\partial\phi_i/\partial z$ and on the derivatives $\partial\mu_i/\partial\phi_j$, which can be written explicitly.

## 5.1 Full expression for $\partial\mu_i/\partial\phi_j$

Starting from Equation 17, the partial derivatives can be written as

$$\begin{aligned}\beta\frac{\partial\mu_i^{\mathrm{exc}}}{\partial\phi_j} &= -\frac{6{\sigma_i}^3\xi_2}{\phi^4}\ln\left(1-\phi\right)\left(\xi_2\phi\left(\frac{1}{\sigma_i}+\frac{1}{\sigma_j}\right)-{\xi_2}^2-\frac{\phi^2}{\sigma_i\sigma_j}\right) \\ &\quad +\frac{3\sigma_i/\sigma_j+3(\sigma_i/\sigma_j)^2+(\sigma_i/\sigma_j)^3}{1-\phi}+\frac{3\xi_2\sigma_i+3\xi_1{\sigma_i}^2+\xi_0{\sigma_i}^3}{(1-\phi)^2} \\ &\quad +\frac{\phi^2}{(1-\phi)^4}\left(\frac{3\xi_1{\sigma_i}^3}{\sigma_j}+\frac{3\xi_2{\sigma_i}^3}{{\sigma_j}^2}\right) \\ &\quad +\frac{\phi}{(1-\phi)^4}\left({\xi_2}^2{\sigma_i}^2\left(3-\frac{6\xi_1\sigma_i}{\xi_2}\right)+\frac{3\xi_2{\sigma_i}^2(2-2\xi_1\sigma_i+\xi_2\sigma_i)}{\sigma_j}-\frac{6\xi_2{\sigma_i}^3}{{\sigma_j}^2}\right) \\ &\quad +\frac{1}{(1-\phi)^4}\left({\xi_2}^2{\sigma_i}^2\left(\frac{6\xi_1\sigma_i}{\xi_2}-5\xi_2\sigma_i-18\right)+\frac{3\xi_1{\sigma_i}^3-12\xi_2{\sigma_i}^2-18{\xi_2}^2{\sigma_i}^3}{\sigma_j}+\frac{3\xi_2{\sigma_i}^3}{{\sigma_j}^2}\right) \\ &\quad +\frac{1}{\phi(1-\phi)^4}\left({\xi_2}^2{\sigma_i}^2(26\xi_2\sigma_i+21)+\frac{6\xi_2{\sigma_i}^2+21{\xi_2}^2{\sigma_i}^3}{\sigma_j}\right) \\ &\quad +\frac{1}{\phi^2(1-\phi)^4}\left(-{\xi_2}^2{\sigma_i}^2(21\xi_2\sigma_i+6)-\frac{6{\xi_2}^2{\sigma_i}^3}{\sigma_j}\right)+\frac{6{\xi_2}^3{\sigma_i}^3}{\phi^3(1-\phi)^4}\ .\end{aligned} \tag{30}$$

In addition, $\beta\mu_i^{\mathrm{id}} = (1/\phi_i)(\partial\phi_i/\partial z)$, hence, $\partial\mu_i^{\mathrm{id}}/\partial\phi_j = 0$, for $i\neq j$, and $\partial\mu_i/\partial\phi_j = \partial\mu_i^{\mathrm{ex}}/\partial\phi_j$.

In the tracer limit, with one majority component (the volume fractions of all other components $i$ can be neglected compared to the volume fraction of the majority component, $\phi_i \ll \phi$, we write $\alpha_i = \sigma_i/\sigma$, with $\sigma$ the diameter of the particles of the majority species, and thus $\partial\mu_i^{\mathrm{exc}}/\partial\phi$ can be written analytically as follows:

$$\beta\frac{\partial\mu_i^{\mathrm{exc}}}{\partial\phi} = \frac{6\alpha_i^3+2\alpha_i^3(3-2\alpha_i)(1-\phi)+3\alpha_i(1-\alpha_i^2)(1-\phi)^2+(2\alpha_i^3-3\alpha_i^2+1)(1-\phi)^3}{(1-\phi)^4} \tag{31}$$

which, for $\alpha = 1$ simplifies to the derivative of the Carnahan-Starling equation of state (see also eq. A9 in Ref. [5]):

$$\beta \left.\frac{\partial \mu^{\mathrm{exc}}}{\partial \phi}\right|_{\alpha=1} = \frac{8-2\phi}{(1-\phi)^4} \,. \tag{32}$$

Using this expression in Equation 31, we find that the particle volume fraction of the majority particles at the maximum in the distribution of one of the tracer particles $i$ is given by Equation 4.11 in the main text (with $\alpha_i = \alpha$ and $\phi_2^* = \phi$). Alternatively, $\partial\mu_1^{\mathrm{exc}}/\partial\phi_2$ can be approximated by a series of powers (Equation 4.8 in the main text) and the expression for $\phi^*$ becomes:

$$\frac{L_{\mathrm{g},2}}{L_{\mathrm{g},1}} = \alpha^3 \phi_2^{\mathrm{iso}} = \frac{\sum_{\lambda=1}^{\infty} \Big[(1+\lambda\alpha)^3 + 3(\lambda-1)\alpha^2 + (\lambda-1)(\lambda-2)\alpha^3\Big] {\phi_2^*}^{\lambda}}{1 + (8\phi_2^* - 2{\phi_2^*}^2)(1-\phi_2^*)^{-4}} \,. \tag{33}$$

## 5.2 Two-component mixtures

We abbreviate $\beta\partial\mu_i^{\mathrm{ex}}/\partial\phi_j$ as $\mu_{ij}$. Please note that this definition of $\mu_{ij}$ differs slightly from the definition used in the main text, for reasons of clarity of the equations below. In a two-component mixture, two differential equations with two unknown density gradients define the sedimentation profile.

$$\frac{1}{\phi_1}\frac{\partial\phi_1}{\partial z} + \mu_{11}\frac{\partial\phi_1}{\partial z} + \mu_{12}\frac{\partial\phi_2}{\partial z} = -\frac{1}{L_{\mathrm{g},1}} \tag{34}$$

$$\frac{1}{\phi_2}\frac{\partial\phi_2}{\partial z} + \mu_{21}\frac{\partial\phi_1}{\partial z} + \mu_{22}\frac{\partial\phi_2}{\partial z} = -\frac{1}{L_{\mathrm{g},2}} \tag{35}$$

After rewriting, we obtain:

$$\frac{\partial\phi_1}{\partial z} = \left(-\frac{1}{L_{\mathrm{g},1}} + \frac{\mu_{12}}{L_{\mathrm{g},2}(1/\phi_2 + \mu_{22})}\right)\left(\frac{1}{\phi_1} + \mu_{11} - \frac{\mu_{12}\mu_{21}}{1/\phi_2 + \mu_{22}}\right)^{-1} \tag{36}$$

$$\frac{\partial\phi_2}{\partial z} = \left(-\frac{1}{L_{\mathrm{g},2}} + \frac{\mu_{21}}{L_{\mathrm{g},1}(1/\phi_1 + \mu_{11})}\right)\left(\frac{1}{\phi_2} + \mu_{22} - \frac{\mu_{21}\mu_{12}}{1/\phi_1 + \mu_{11}}\right)^{-1} \approx -\frac{1}{L_{\mathrm{g},2}(1/\phi_2 + \mu_{22})} \tag{37}$$

where the second (approximate) identity hold for the majority species in the tracer limit. These direct differential equations can be solved by standard numerical integration techniques.

## 5.3 Three-component mixtures

In a three-component mixture, three differential equations with three unknown density gradients define the sedimentation profile.

$$\frac{1}{\phi_1}\frac{\partial\phi_1}{\partial z} + \mu_{11}\frac{\partial\phi_1}{\partial z} + \mu_{12}\frac{\partial\phi_2}{\partial z} + \mu_{13}\frac{\partial\phi_3}{\partial z} = -\frac{1}{L_{\mathrm{g},1}} \tag{38}$$

$$\frac{1}{\phi_2}\frac{\partial\phi_2}{\partial z} + \mu_{21}\frac{\partial\phi_1}{\partial z} + \mu_{22}\frac{\partial\phi_2}{\partial z} + \mu_{23}\frac{\partial\phi_3}{\partial z} = -\frac{1}{L_{\mathrm{g},2}} \tag{39}$$

$$\frac{1}{\phi_3}\frac{\partial\phi_3}{\partial z} + \mu_{31}\frac{\partial\phi_1}{\partial z} + \mu_{32}\frac{\partial\phi_2}{\partial z} + \mu_{33}\frac{\partial\phi_3}{\partial z} = -\frac{1}{L_{\mathrm{g},3}} \tag{40}$$

We abbreviate $(1/\phi_i + \mu_{ii})$ as $\mu_i^*$. After rewriting, we obtain:

$$\frac{\partial\phi_1}{\partial z} = \frac{L_{\mathrm{g},1}^{-1}(\mu_{23}\mu_{32} - \mu_2^*\mu_3^*) \;+\; L_{\mathrm{g},2}^{-1}(\mu_3^*\mu_{12} - \mu_{13}\mu_{32}) \;+\; L_{\mathrm{g},3}^{-1}(\mu_2^*\mu_{13} - \mu_{12}\mu_{23})}{\mu_1^*(\mu_2^*\mu_3^* - \mu_{23}\mu_{32}) \;+\; \mu_{12}(\mu_{23}\mu_{31} - \mu_3^*\mu_{21}) \;+\; \mu_{13}(\mu_{21}\mu_{32} - \mu_2^*\mu_{31})} \tag{41}$$

$$\frac{\partial\phi_2}{\partial z} = \frac{L_{\mathrm{g},1}^{-1}(\mu_3^*\mu_{21} - \mu_{23}\mu_{31}) \;+\; L_{\mathrm{g},2}^{-1}(\mu_{13}\mu_{31} - \mu_1^*\mu_3^*) \;+\; L_{\mathrm{g},3}^{-1}(\mu_1^*\mu_{23} - \mu_{13}\mu_{21})}{\mu_2^*(\mu_1^*\mu_3^* - \mu_{13}\mu_{31}) \;+\; \mu_{21}(\mu_{12}\mu_{32} - \mu_3^*\mu_{12}) \;+\; \mu_{23}(\mu_{12}\mu_{31} - \mu_1^*\mu_{32})} \tag{42}$$

$$\frac{\partial\phi_3}{\partial z} = \frac{L_{\mathrm{g},1}^{-1}(\mu_2^*\mu_{31} - \mu_{21}\mu_{32}) \;+\; L_{\mathrm{g},2}^{-1}(\mu_1^*\mu_{32} - \mu_{31}\mu_{12}) \;+\; L_{\mathrm{g},3}^{-1}(\mu_{12}\mu_{21} - \mu_1^*\mu_2^*)}{\mu_3^*(\mu_1^*\mu_2^* - \mu_{12}\mu_{21}) \;+\; \mu_{31}(\mu_{12}\mu_{23} - \mu_2^*\mu_{13}) \;+\; \mu_{32}(\mu_{21}\mu_{13} - \mu_1^*\mu_{23})} \tag{43}$$

## 6 Force balance in a centrifugal field

Starting from Equation 51 in the main text, we obtain the following force balance for a one-component suspension in sedimentation-diffusion equilibrium in a centrifugal field (incompressible particles and fluid)

$$F_i^{\mathrm{tot}} = 0 = \frac{v_\mathrm{c}(\rho_\mathrm{c} - \rho_\mathrm{F})\omega^2 r}{k_\mathrm{B}T} = -\frac{1}{\phi}\frac{\partial\phi}{\partial r} - \beta\frac{\partial\mu_i^{\mathrm{ex}}}{\partial\phi}\frac{\partial\phi}{\partial r} \tag{44}$$

$$\frac{\partial\phi}{\partial r^2} = -\frac{2v_\mathrm{c}(\rho_\mathrm{c} - \rho_\mathrm{F})\omega^2}{k_\mathrm{B}T}\left(\frac{1}{\phi} + \frac{\partial\mu_\mathrm{c}^{\mathrm{ex}}}{\partial\phi}\right)^{-1} \tag{45}$$

$$\frac{\partial\phi}{\partial r^2} = -\frac{2}{{L_\omega}^2}\left(\frac{\phi}{1 + \frac{8\phi - 2\phi^2}{(1-\phi)^4}}\right) . \tag{46}$$

In Equation 46 we inserted the Carnahan-Starling equation of state for hard spheres.

## 7 Sedimentation coefficient in a one-component suspension

We start from Equation 55 in the main text, and insert an expression for the fluid velocity in single component suspensions of hard spheres from Equation 29 in the main text:

$$s_i = \frac{\mathbf{v}_\mathrm{c}}{\omega^2 r} \approx \beta D_\mathrm{c}\, v_\mathrm{c}(\rho_\mathrm{c} - \rho_{\mathrm{susp}}) - \frac{\phi}{1-\phi}\frac{\mathbf{v}_\mathrm{c}}{\omega^2 r} \tag{47}$$

$$= \beta D_\mathrm{c}\, v_\mathrm{c}(1-\phi)^2(\rho_\mathrm{c} - \rho_\mathrm{F}) . \tag{48}$$

## 8 Equations of state for mixtures of rods and disks

For rods we may use the analytical 1-D equation of state of Tonks gas [6].

$$\frac{\mu_{\mathrm{rod}}^{\mathrm{ex}}}{k_\mathrm{B}T} = \ln\left(\frac{1}{1-\eta}\right) + \frac{\eta}{1-\eta} \tag{49}$$

where $\eta$ is the line fraction (1-D analogue of the volume fraction). This EOS is expected to yield realistic results for very long rods, which are forced to orient themselves in the direction of gravity as they sediment, due to the high flow resistance in any other orientation.

For (mixtures of) disks, we may use the empirical 2-D equation of state of Boublik, which was recently reported [7].

$$\frac{\mu_i^{\mathrm{ex}}}{k_\mathrm{B}T} = A_{\mathrm{c},i}\left(\frac{1 + \gamma_\mathrm{s} + \gamma_\mathrm{s}^2\, y/7}{1-y} + \frac{\gamma_\mathrm{s}\, y(1 + \gamma_\mathrm{s}\, y/14)}{(1-y)^2}\right) \tag{50}$$

where $y$ is the 2-D filling fraction, $A_{c,i}$ is area of the disk, $R_{c,i}$ is the mean radius (perimeter divided by $2\pi$) and $\gamma_s$ is given by

$$\gamma_s = \frac{\pi \sum_i x_i {R_{c,i}}^2}{\sum_i x_i A_{c,i}} \tag{51}$$

# 9 Movies

The following set of movies is available as Supporting Information:

1. tracer_A_dpmma_yz_5fps.mp4
   (see also Figure 2A) Sedimentation dynamic of a bidisperse suspension of hard spheres with one majority particle (left panel, blue line: MFA, $\sigma_2$ = 180 nm, $\rho_2$ = 2.14 g/cm$^3$, $\phi_2$ at $t = 0$ is 0.15) and one particle present in trace amounts (right panel, red line: d-PMMA, $\sigma_1$ = 1.0 µm, $\rho_1$ = 1.28 g/cm$^3$, $\phi_1$ at $t = 0$ is $10^{-4}$) in a mixture of urea and water ($\rho_F$ = 1.04 g/cm$^3$) as solvent. The tracer particles have a higher density than the homogeneous suspension ($\rho_{susp}$ at $t = 0$ is 1.20 g/cm$^3$). Progress of time is indicated in the left panel in seconds.

2. tracer_A_dpmma_zy_5fps.mp4
   Same as movie [tracer_A_dpmma_yz_5fps.mp4], but with $\phi$ plotted on the $x$-axis and height plotted on the $y$-axis.

3. tracer_B_pmma_yz_5fps.mp4
   (see also Figure 2B) Sedimentation dynamic of a bidisperse suspension of hard spheres with one majority particle (left panel, blue line: MFA, $\sigma_2$ = 180 nm, $\rho_2$ = 2.14 g/cm$^3$, $\phi_2$ at $t = 0$ is 0.15) and one particle present in trace amounts (right panel, red line: PMMA, $\sigma_1$ = 1.0 µm, $\rho_1$ = 1.19 g/cm$^3$, $\phi_1$ at $t = 0$ is $10^{-4}$) in a mixture of urea and water ($\rho_F$ = 1.04 g/cm$^3$) as solvent. The tracer particles have almost the same density as the homogeneous suspension ($\rho_{susp}$ at $t = 0$ is 1.20 g/cm$^3$). Progress of time is indicated in the left panel in seconds.

4. tracer_B_pmma_zy_5fps.mp4
   Same as movie [tracer_B_dpmma_yz_5fps.mp4], but with $\phi$ plotted on the $x$-axis and height plotted on the $y$-axis.

5. tracer_C_pema_yz_5fps.mp4
   (see also Figure 2C) Sedimentation dynamic of a bidisperse suspension of hard spheres with one majority particle (left panel, blue line: MFA, $\sigma_2$ = 180 nm, $\rho_2$ = 2.14 g/cm$^3$, $\phi_2$ at $t = 0$ is 0.15) and one particle present in trace amounts (right panel, red line: PEMA, $\sigma_1$ = 1.0 µm, $\rho_1$ = 1.12 g/cm$^3$, $\phi_1$ at $t = 0$ is $10^{-4}$) in a mixture of urea and water ($\rho_F$ = 1.04 g/cm$^3$) as solvent. The tracer particles have a lower density than the homogeneous suspension ($\rho_{susp}$ at $t = 0$ is 1.20 g/cm$^3$). Progress of time is indicated in the left panel in seconds.

6. tracer_C_pema_zy_5fps.mp4
   Same as movie [tracer_C_dpmma_yz_5fps.mp4], but with $\phi$ plotted on the $x$-axis and height plotted on the $y$-axis.

7. flag_A_yz_8fps.mp4
   (see also Figure 3a) Sedimentation dynamics of a three-component mixture of hard spheres with $\sigma_1$ = 200 nm, $\rho_1$ = 2.20 g/cm$^3$ (left panel, red line); $\sigma_2$ = 360 nm, $\rho_2$ = 1.35 g/cm$^3$ (middle panel, blue line); $\sigma_3$ = 600 nm and $\rho_3$ = 1.05 g/cm$^3$ (right panel, green line). All three components have an average volume fraction of $\phi_0$ = 7.5%. The solvent is water with $\rho_F$ = 1.00 g/cm$^3$ and the total sedimentation profiles extends approximately 3 mm. Progress of time is indicated in the left panel in seconds.

8. flag_A_zy_8fps.mp4
   Same as movie [flag_A_yz_8fps.mp4], but with $\phi$ plotted on the $x$-axis and height plotted on the $y$-axis.

9. flag_A_color_rwb_withtext.mp4
   Same as movie [flag_A_yz_8fps.mp4], but visualized using three different colors: blue for component 1, white for component 2 and red for component 3. The brightness of the colors is a measure for the concentration of particles.

10. flag_B_yz_8fps.mp4
Sedimentation dynamics of a three-component mixture of hard spheres with $\sigma_1 = 200$ nm, $\rho_1 = 2.20$ g/cm$^3$ (left panel, red line); $\sigma_2 = 300$ nm, $\rho_2 = 1.30$ g/cm$^3$ (middle panel, blue line); $\sigma_3 = 600$ nm and $\rho_3 = 1.05$ g/cm$^3$ (right panel, green line). All three components have an average volume fraction of $\phi_0 = 5.4\%$. The solvent is a mixture of water and urea with $\rho_\mathrm{F} = 1.04$ g/cm$^3$ and the total sedimentation profiles extends approximately 6 mm. Progress of time is indicated in the left panel in seconds.

11. flag_B_zy_8fps.mp4
Same as movie [flag_B_yz_8fps.mp4], but with $\phi$ plotted on the $x$-axis and height plotted on the $y$-axis.

# References


[1] Guggenheim E A 1967 *Thermodynamics* (North-Holland Publishing Company)
[2] Kops-Werkhoven M, Vrij A and Lekkerkerker H 1983 *Journal of Chemical Physics* **78** 2760–2763
[3] Vrij A 1980 *Journal of Chemical Physics* **72** 3735–3739
[4] Martin M, Hoyos M and Lhuillier D 1994 *Colloid & Polymer Science* **272** 1582–1589
[5] Biesheuvel P M and Lyklema J 2005 *Journal of Physics: Condensed Matter* **17** 6337–6352
[6] Biben T, Hansen J P and Barrat J L 1993 *Journal of Chemical Physics* **98** 7330–7344
[7] Boublik T 2011 *Molecular Physics* **109** 1575–1580