Nonequilibrium interactions between multi-scale colloids regulate the suspension microstructure and rheology

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1 Smoluchowski Equation derivation

We begin with a general Smoluchowski equation governing the total probability density $P_{\mathrm{N+2}}(\mathbf{x}_1,...,\mathbf{x}_{\mathrm{N+2}},t)$:

$$\frac{\partial P_{\mathrm{N+2}}}{\partial t}+\sum_{i=1}^{\mathrm{N+2}}\nabla_i\cdot\mathbf{j}_i=0. \tag{1.1}$$

Here, $i=1$ refers to the probe, $i=2$ is the quiescent colloid, and $i=3,...,N+2$ are the N depletant particles. We will refer to all particle positions relative to the probe particle, $\mathbf{r}_i=\mathbf{x}_i-\mathbf{x}_1$. Using chain rule, all derivatives are taken with respect to the relative coordinate r_i, and the absolute position of the probe does not matter. The relative particle translational flux is given by $\mathbf{j}_i=(\mathbf{j}_i-\mathbf{j}_1)=\mathbf{U}_iP_{\mathrm{N}}$ where $\mathbf{U}_i$ is the particle velocity.

In a suspension, particles move under the action of external forces $\mathbf{F}^{\mathrm{ext}}$, interparticle forces $\mathbf{F}^{\mathrm{P}}$, and entropic or thermal forces $k_{\mathrm{B}}T\nabla\ln P_{\mathrm{N+2}}$, such that the particle velocity may be expressed as:

$$\mathbf{U}_i=\sum_{j=1}^{\mathrm{N+2}}[\mathbf{M}_{ij}\cdot(\mathbf{F}_j^{\mathrm{ext}}+\mathbf{F}_j^{\mathrm{P}})-\mathbf{D}_{ij}\cdot\nabla_j\ln P_N] \tag{1.2}$$

The hydrodynamic mobility tensor, $\mathbf{M}_{ij}=(k_{\mathrm{B}}T)^{-1}\mathbf{D}_{ij}$, couples a force exerted on particle j to the velocity of particle i, where $\mathbf{D}_{ij}$ is the diffusion coefficient. Neglecting hydrodynamic interactions, the diffusivity is isotropic and constant, such that $\mathbf{M}_{ij}=\delta_{ij}\zeta_{ij}^{-1}$. The drag coefficients for colloids and depletants are given by ζ_{c} and ζ_{b}, respectively.

We observe that the many-body probability density P_{N+2} can be re-expressed as a product of conditional probabilities or distributions, $P_1P_{1|1}P_{1|2}...P_{1|N+1}$. By definition, $P_{1|n}$ is the conditional probability of finding the $n+1$-th particle given the positions of the previous n particles.

Assuming the depletant particles are statistically homogeneous and indistinguishable, we integrate Eq. 1.1- 1.2 over the $N-1$ depletant particles:

$$\frac{\partial(P_{1|1}P_{1|2})}{\partial t}+\nabla\cdot\langle\mathbf{j}_2-\mathbf{j}_1\rangle_3+\nabla_{\mathbf{h}}\cdot\langle\mathbf{j}_3-\mathbf{j}_1\rangle_3=0 \tag{1.3}$$

where the averaged colloidal and depletant fluxes are given by:

$$\langle\mathbf{j}_2-\mathbf{j}_1\rangle_3=-\mathbf{U}_1P_{1|1}P_{1|2}+\int\left[\mathbf{M}_{22}P_{\mathrm{N+1}|1}\cdot\mathbf{F}_2^P-\mathbf{D}_{22}\cdot\nabla P_{\mathrm{N+1}|1}\right]d\mathbf{r}_4...d\mathbf{r}_{\mathrm{N+2}} \tag{1.4}$$

and:

$$\langle\mathbf{j}_3-\mathbf{j}_1\rangle_3=-\mathbf{U}_1P_{1|1}P_{1|2}+\int\left[\mathbf{M}_{33}P_{\mathrm{N+1}|1}\cdot\mathbf{F}_3^P-\mathbf{D}_{33}\cdot\nabla_{\mathbf{h}}P_{\mathrm{N+1}|1}\right]d\mathbf{r}_4...d\mathbf{r}_{\mathrm{N+2}}. \tag{1.5}$$

Note that $P_{1|1}(\mathbf{r},t)$ is the probability of finding the quiescent colloid at position $\mathbf{r}$ and $P_{1|2}(\mathbf{h},t|\mathbf{r})$ is the probability of finding a depletant particle at $\mathbf{h}$ given that the quiescent colloid is at $\mathbf{r}$. To be consistent with the main text, we have re-defined the quiescent colloid position as $\mathbf{r}=\mathbf{r}_2$ and the depletant degree of freedom as $\mathbf{h}=\mathbf{r}_3$ for clarity. Furthermore, indices on gradients with respect to $\mathbf{r}$ have been omitted. Note that $P_{\mathrm{N+2}}=P_{\mathrm{N+1}|1}P_1$ and that the absolute position of the probe, P_1, does not matter.

We will now consider the relative colloidal flux. Replacing the interparticle forces with derivatives of the log of the equilibrium Boltzmann distribution, $\mathbf{F}_i^P=-\nabla_iV^{\mathrm{TOT}}\sim k_{\mathrm{B}}T\nabla_i\ln P_{\mathrm{N+1}|1}^{\mathrm{eq}}$, we obtain:

$$\langle\mathbf{j}_2-\mathbf{j}_1\rangle_3=-\mathbf{U}_1P_{1|1}P_{1|2}+\int\left[\mathbf{D}_{22}\cdot P_{\mathrm{N+1}|1}\nabla\ln\frac{P_{\mathrm{N+1}|1}^{\mathrm{eq}}}{P_{\mathrm{N+1}|1}}\right]d\mathbf{r}_4...d\mathbf{r}_{\mathrm{N+2}} \tag{1.6}$$

Substitution of this expansion into Eq. 1.1 results in the BBGKY hierarchy of equations, which quickly becomes analytically intractable for many particles. A closure is sought by diluteness of the bath particles, replacing $(P^{\text{eq}}_{\text{N}+1|1})/(P_{\text{N}+1|1})$ with $(P^{\text{eq}}_{1|1}P^{\text{eq}}_{1|2})/(P_{1|1}P_{1|2})$ as all neglected terms are $O(n_{\text{b}})$. From this, we obtain:

$$\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3 = -\mathbf{U}_1 P_{1|1}P_{1|2} + \mathbf{D}_{22}\cdot P_{1|1}P_{1|2}\nabla \ln\left[\frac{P^{\text{eq}}_{1|1}P^{\text{eq}}_{1|2}}{P_{1|1}P_{1|2}}\right]. \tag{1.7}$$

Analogously, the depletant flux becomes:

$$\langle \mathbf{j}_3 - \mathbf{j}_1 \rangle_3 = -\mathbf{U}_1 P_{1|1}P_{1|2} + \mathbf{D}_{33}\cdot P_{1|1}P_{1|2}\nabla_{\mathbf{h}} \ln\left[\frac{P^{\text{eq}}_{1|1}P^{\text{eq}}_{1|2}}{P_{1|1}P_{1|2}}\right]. \tag{1.8}$$

We apply the Boltzmann relation, $P^{\text{eq}}_{1|1} \sim e^{-V_{21}/k_{\text{B}}T}$ and $P^{\text{eq}}_{1|2} \sim e^{-(V_{31}+V_{32})/k_{\text{B}}T}$ where the two-body potentials are defined $V_{21} = V_{21}(\mathbf{r})$, $V_{31} = V_{31}(\mathbf{h})$, and $V_{32} = V_{32}(\mathbf{h}-\mathbf{r})$. The fluxes reduce to:

$$\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3 = -\mathbf{U}_1 P_{1|1}P_{1|2} - \mathbf{D}_{22}\cdot\left[(\nabla P_{1|1}P_{1|2}) + P_{1|1}P_{1|2}\nabla V_{21}/(k_{\text{B}}T) + P_{1|1}P_{1|2}\nabla V_{32}/(k_{\text{B}}T)\right] \tag{1.9}$$

$$\langle \mathbf{j}_3 - \mathbf{j}_1 \rangle_3 = -\mathbf{U}_1 P_{1|1}P_{1|2} - \mathbf{D}_{33}\cdot\left[(\nabla_{\mathbf{h}} P_{1|1}P_{1|2}) + P_{1|1}P_{1|2}\nabla_{\mathbf{h}} V_{31}/(k_{\text{B}}T) + P_{1|1}P_{1|2}\nabla_{\mathbf{h}} V_{32}/(k_{\text{B}}T)\right] \tag{1.10}$$

we can relate these conditional probabilities physical quantities by $P_{1|1} = n_{\text{c}}g$ and $P_{1|2} = n_{\text{b}}\rho$ where g is simply the colloidal pair distribution function and ρ may be thought of as the local depletant structure about the colloidal pair.

The particle velocity is given by $\mathbf{U}_1 = U_{\text{c}}\mathbf{e_x}$. We chose to nondimensionalize all distances by the depletant size d_{b}, energy by $k_{\text{B}}T$, and time by the Brownian timescale of the depletant particle, $\tau^b_{\text{c}} = d^2_{\text{b}}/D_{\text{b}}$. We recover a final nondimensional Smoluchowski equation, averaged over $N-1$ depletants:

$$\frac{\partial (g\rho)}{\partial t} + \nabla\cdot\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3 + \nabla_{\mathbf{h}}\cdot\langle \mathbf{j}_3 - \mathbf{j}_1 \rangle_3 = 0 \tag{1.11}$$

where

$$\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3 = -\text{Pe}_{\text{c}}\alpha^{-1}\mathbf{e_x}g\rho - \alpha^{-1}\left[\nabla(g\rho) + g\rho\nabla V_{21}/(k_{\text{B}}T) + g\rho\nabla V_{32}/(k_{\text{B}}T)\right] \tag{1.12}$$

$$\langle \mathbf{j}_3 - \mathbf{j}_1 \rangle_3 = -\text{Pe}_{\text{c}}\alpha^{-1}\mathbf{e_x}g\rho - \left[\nabla_{\mathbf{h}}(g\rho) + g\rho\nabla_{\mathbf{h}} V_{31}/(k_{\text{B}}T) + g\rho\nabla_{\mathbf{h}} V_{32}/(k_{\text{B}}T)\right]. \tag{1.13}$$

We have defined the relative drag ratio $\alpha = D_{\text{b}}/D_{\text{c}}$ and two Péclet Numbers, $\text{Pe}_{\text{c}} = U_{\text{c}}d_{\text{b}}/D_{\text{c}}$ and $\text{Pe}_{\text{b}} = \text{Pe}_{\text{c}}/\alpha = U_{\text{c}}d_{\text{b}}/D_{\text{b}}$ as documented in the main text.

Finally, we may proceed to integrate Eq. 1.11 over the last depletant particle to obtain the governing equation for the quiescent colloid distribution about the probe:

$$\frac{\partial g}{\partial t} + \nabla\cdot\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_2 = 0 \tag{1.14}$$

where the effective colloidal flux is:

$$\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_2 = -\text{Pe}_{\text{c}}\alpha^{-1}\mathbf{e_x}g - \alpha^{-1}\left[\nabla g + g\nabla V_{21}/(k_{\text{B}}T) + g n_{\text{b}}\int \rho\nabla V_{32}/(k_{\text{B}}T)d\mathbf{h}\right]. \tag{1.15}$$

Eq. 1.11-1.13 and Eq. 1.14-1.15 are our main results in this section. In particular, this Smoluchowski framework is general to any three-particle system and may be used for a number of different species and particle interactions. In the next section, we proceed to solve these equations using a perturbation expansion approach.

2 Regular Perturbation Expansion

In the limit where the Brownian timescale of the colloid is very small relative to the Brownian timescale of the smaller depletants ($\alpha \ll 1$), we may perform the following regular perturbation expansion for both the colloidal and depletant structures about the probe.

We expand $g \approx g_0 + \alpha^{-1}g_1 + \alpha^{-2}g_2 + O(\alpha^{-3})$ and $\rho \approx \rho_0 + \alpha^{-1}\rho_1 + \alpha^{-2}\rho_2 + O(\alpha^{-3})$. Observe that, by mass conservation, we have $n_{\text{c}}\int \rho_0 d\mathbf{h} = 1$, $\int \rho_{i\neq 0} d\mathbf{h} = 0$ and similarly for g.

At steady state, the leading order terms of Eq. 1.11-1.13 become:

$$\nabla_{\mathbf{h}}\cdot\left[\nabla_{\mathbf{h}}\rho_0 + \rho_0\nabla_{\mathbf{h}}(V_{31}/(k_{\text{B}}T) + V_{32}/(k_{\text{B}}T))\right] = 0 \tag{2.1}$$

Which is simply diffusion under an external field. From this, it is clear that the diffusion of depletants, under our assumption that $\alpha \ll 1$, is the fastest process in the system. Solved with no flux boundary conditions at contact and unity at $\mathbf{h} \to \infty$, the solution takes on a simple Boltzmann form, $\rho_0 \sim e^{(-V_{32}-V_{31})/(k_B T)}$.

At $O(\alpha^{-1})$, the g_0 governing equation may be obtained from expanding Eq. 1.14- 1.15 as:

$$\nabla \cdot \left[\mathrm{Pe_c} g_0 \mathbf{e_x} + \nabla g_0 + g_0 \nabla V_{21}/(k_B T) - g_0 n_c \int \rho_0 \nabla V_{32}/(k_B T) d\mathbf{h} \right] = 0. \tag{2.2}$$

The first three terms on the RHS exactly match active microrheology of a probe navigating through a monodisperse bath whereas the last term is the potential-of-mean-force contribution from depletants. Because ρ_0 follows a Boltzmann distribution, we find that $\int n_c \int \rho_0 \nabla V_{32}/(k_B T) d\mathbf{h}$ is analogous to an Asakura-Oosawa type depletion potential.

Additionally, at $O(\alpha^{-1})$, it may be shown through that Eq. 1.11- 1.13 becomes:

$$\nabla \rho_0 \cdot \langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3^0 + \nabla_{\mathbf{h}} \cdot [\mathrm{Pe_c} \mathbf{e_x} g_0 \rho_0 - g_0 \rho_1 \nabla_{\mathbf{h}} (V_{31} + V_{32}) - g_0 \nabla_{\mathbf{h}} \rho_1] = 0 \tag{2.3}$$

where the $\langle \mathbf{j}_2 - \mathbf{j}_1 \rangle_3^0$ is equal to the terms in the bracket of Eq. 2.2. We observe that the leading order colloidal flux and colloidal microstructure now contribute to the ρ_1 solution, effectively coupling the local depletant motion to the slower colloidal motion.

Finally, once ρ_1 is known, it is then possible to obtain g_1 through the $O(\alpha^{-2})$ expansion of Eq. 1.14- 1.15:

$$\nabla \cdot \left[\mathrm{Pe_c} g_1 \mathbf{e_x} + \nabla g_1 + g_1 \nabla V_{21}/(k_B T) - g_1 n_c \int \rho_1 \nabla V_{32}/(k_B T) d\mathbf{h} \right] = 0. \tag{2.4}$$

3 Microviscosity Calculation

We follow the approach of Squires and Brady, beginning with the total drag force experienced by the probe colloid due to external driving, thermal forces, and interactions with the particles in suspension:

$$\mathbf{F}_1 = \mathbf{M}_{11}^{-1} \cdot U_1 \mathbf{e_x} + \sum_{j=1}^{N+2} \mathbf{M}_{11}^{-1} \cdot (\mathbf{D}_{1j} - \mathbf{D}_{11}) \cdot \nabla_j \ln(P_{N+2}/P_{N+2}^{eq}) \tag{3.1}$$

Neglecting hydrodynamic interactions as we have done before, we have:

$$\mathbf{F}_1 = k_B T D_{11}^{-1} U_1 \mathbf{e_x} - \sum_{j=2}^{N+2} k_B T \nabla_j \ln(P_{N+2}/P_{N+2}^{eq}). \tag{3.2}$$

Similar to the previous section, we use a diluteness closure to replace P_{N+2}/P_{N+2}^{eq} with $(P_{1|1}P_{1|2})/(P_{1|1}^{eq}P_{1|2}^{eq})$. We now perform an average over $N-1$ depletant particles,

$$\langle \mathbf{F}_1 \rangle_3 = \int \mathbf{F}_1 P_{N-1|3} d\mathbf{r}_4 ... d\mathbf{r}_{N+2} \tag{3.3}$$

which recovers:

$$\langle \mathbf{F}_1 \rangle_3 = k_B T D_{11}^{-1} U_1 \mathbf{e_x} P_{1|1} P_{1|2} - k_B T P_{1|1} P_{1|2} \nabla \ln \left[\frac{P_{1|1} P_{1|2}}{P_{1|1}^{eq} P_{1|2}^{eq}} \right] - k_B T P_{1|1} P_{1|2} \nabla_{\mathbf{h}} \ln \left[\frac{P_{1|1} P_{1|2}}{P_{1|1}^{eq} P_{1|2}^{eq}} \right]. \tag{3.4}$$

Substituting the Boltzmann relations, $P_{1|1}^{eq} \sim e^{-V_{21}/k_B T}$ and $P_{1|2}^{eq} \sim e^{-(V_{31}+V_{32})/k_B T}$, we obtain:

$$\langle \mathbf{F}_1 \rangle_3 = k_B T D_{11}^{-1} U_1 \mathbf{e_x} P_{1|1} P_{1|2} - k_B T \nabla (P_{1|1} P_{1|2}) + k_B T P_{1|1} P_{1|2} \nabla (V_{21} + V_{32}) - k_B T \nabla_{\mathbf{h}} (P_{1|1} P_{1|2}) + k_B T P_{1|1} P_{1|2} \nabla_{\mathbf{h}} (V_{31} + V_{32}) \tag{3.5}$$

Integrating over the last depletant and the colloidal degrees of freedom($\int ... d\mathbf{h} d\mathbf{r}$) and noting that $n_b \int \rho d\mathbf{h} = 1$, we obtain:

$$\begin{aligned} \langle \mathbf{F}_1 \rangle_1 = & k_B T D_{11}^{-1} U_1 \mathbf{e_x} + k_B T n_c \int g \nabla V_{21} d\mathbf{r} + k_B T n_c n_\rho \int g \int \rho \nabla V_{32} d\mathbf{h} d\mathbf{r} \\ & + k_B T n_c n_\rho \int g \int \rho \nabla_{\mathbf{h}} V_{32} d\mathbf{h} d\mathbf{r} + k_B T n_c n_\rho \int g \int \rho \nabla_{\mathbf{h}} V_{31} d\mathbf{h} d\mathbf{r} \end{aligned} \tag{3.6}$$

Note that the third and fourth terms on the RHS cancel since $\nabla V_{32}(\mathbf{r}-\mathbf{h}) = \nabla_{\mathbf{h}} V_{32}(\mathbf{r}-\mathbf{h})$. Nondimensionalizing forces by $k_B T/d_b$ and distances by d_b, we obtain the final form of the force velocity relation for the probe particle:

$$\langle \mathbf{F}_1 \rangle_1 = k_B T D_{11}^{-1} d_b U_1 \mathbf{e_x} + n_c k_B T \int g \nabla V_{21} d\mathbf{r} + n_c n_\rho k_B T \int g \int \rho \nabla_{\mathbf{h}} V_{31} d\mathbf{h} d\mathbf{r} \tag{3.7}$$

Eq. 3.7 is the main result of this section and highlights the $O(n_\mathrm{b})$ contribution to the drag force of the probe. Using this expression, the effective viscosity η due to particles in suspension may be expressed through a Stokes relation, $\langle \mathbf{F}_1 \rangle_1 = 3\pi \eta_\mathrm{eff} d_\mathrm{c} \mathbf{U}_\mathrm{c}$. We find that the effective viscosity of the suspension is given by:

$$\eta_\mathrm{eff} = \eta + \frac{n_\mathrm{c} k_\mathrm{B} T}{3\pi d_\mathrm{c} U_\mathrm{c}} \int g \nabla V_{21} d\mathbf{r} + \frac{n_\mathrm{c} n_\mathrm{b} k_\mathrm{B} T}{3\pi d_\mathrm{c} U_\mathrm{c}} \int g \int \rho \nabla_\mathrm{h} V_{31} d\mathbf{h} d\mathbf{r}. \tag{3.8}$$

From this, the relative microviscosity increment, $\Delta\eta_\mathrm{eff}/\eta = (\eta_\mathrm{eff} - \eta)/\eta$ is exactly as given in the main text.

To further elucidate this interaction, we subsitute our perturbation expansion of ρ and group terms in order of their contributions:

$$\eta_\mathrm{eff} = \eta + \frac{n_\mathrm{c} k_\mathrm{B} T}{3\pi d_\mathrm{c} U_\mathrm{c}} \int g \nabla V_{21} d\mathbf{r} + \frac{n_\mathrm{c} n_\mathrm{b} k_\mathrm{B} T}{3\pi d_\mathrm{c} U_\mathrm{c}} \int g \int \rho_0 \nabla_\mathrm{h} V_{31} d\mathbf{h} d\mathbf{r} + \alpha^{-1} \frac{n_\mathrm{c} n_\mathrm{b} k_\mathrm{B} T}{3\pi d_\mathrm{c} U_\mathrm{c}} \int g \int \rho_1 \nabla_\mathrm{h} V_{31} d\mathbf{h} d\mathbf{r}. \tag{3.9}$$

Note that the second and third terms on the RHS of this equation both contain isotropic forces and are leading order contributions to the microviscosity.

4 Nonequiilbrium pair potential

We will now show how the Smoluchowski framework enables the calculation of an effective, out-of-equilibrium pair potential between the colloidal particles which may be used in many-body systems. We will consider colloids and depletants as perfect hard-spheres that experience no pairwise interactions ($V_{31}, V_{32} = 0$) except a no-flux condition at contact. To make analytical progress, we assume that the driving force is much weaker relative to the diffusion of the depletant particle, allowing a second perturbation expansion in orders of Pe_c:

$$\begin{aligned} \rho_0 &= \rho_{0,0} + \rho_{0,1} \mathrm{Pe}_\mathrm{c} + O\left(\mathrm{Pe}_\mathrm{c}^2\right) \\ g_0 &= g_{0,0} + g_{0,1} \mathrm{Pe}_\mathrm{c} + O\left(\mathrm{Pe}_\mathrm{c}^2\right). \end{aligned} \tag{4.1}$$

Following the regular perturbation approach, $\rho_{0,0}$ is given by a Laplace equation with no-flux boundary conditions, which has the trivial solution that $\rho_{0,0}(\mathbf{h}|\mathbf{r}) = 1$ for all $|\mathbf{r}\text{-}\mathbf{h}| \geq (1 + d_\mathrm{c}/d_\mathrm{b})/2$ and $|\mathbf{h}| \geq (1 + d_\mathrm{c}/d_\mathrm{b})/2$.

Because advection is weak, the leading order equation for $g_{0,0}$ contains just the diffusive and interparticle contributions:

$$\nabla \cdot \left[\nabla g_{0,0} - g_{0,0} n_\mathrm{c} \int \rho_{0,0} \mathbf{e}_{\mathbf{r}\text{-}\mathbf{h}} \delta \left(|\mathbf{r}\text{-}\mathbf{h}| - \frac{(1 + d_\mathrm{c}/d_\mathrm{b})}{2} \right) d\mathbf{h} \right] = 0. \tag{4.2}$$

The Dirac delta function originates from the hard sphere potential at contact. From a simple geometric argument, the integral range reduces to integration along the major arc length around two overlapping circles centered at the origin and $\mathbf{r}$, each with radius $1 + \frac{d_\mathrm{c}}{d_\mathrm{b}}$. The solution to Eq. 4.2 is an isotropic, Boltzmann form $g_{0,0} \sim e^{-V_\mathrm{eq}(r)/k_\mathrm{B}T}$ where V_eq is equivalent to the Asakura-Oosawa potential.

The governing equation for $\rho_{0,1}$ contains advective and diffusive contributions:

$$\nabla_\mathbf{h} \cdot [\mathrm{Pe}_\mathrm{c} \rho_{0,0} \mathbf{e_x} + \nabla_\mathrm{h} \rho_{0,1}] = 0 \tag{4.3}$$

and satisfying no-flux boundary conditions as before. The solution is a simple dipolar distribution that is similar to active microrheology through a monodisperse bath, $\rho_{0,1} = 1 + \mathrm{Pe}_\mathrm{c} h_x/(2h^3)$ for all $|\mathbf{r}\text{-}\mathbf{h}| \geq (1 + d_\mathrm{c}/d_\mathrm{b})/2$ and $|\mathbf{h}| \geq (1 + d_\mathrm{c}/d_\mathrm{b})/2$. From this, we can compute the effective force exerted by the depletants and obtain a potential of mean force by integrating the force to a position r from infinitely-far separation distances. Along the leading front of the probe, we obtain the following simplified form of the nonequilibrium potential between colloidal particles due to interactions with depletant:

$$V_\mathrm{neq}(r; Pe, \alpha) = \int_\infty^r \int_{\theta_1}^{\theta_2} \frac{(1 + \frac{d_\mathrm{c}}{d_\mathrm{b}}) \left[\left(1 + \frac{d_\mathrm{c}}{d_\mathrm{b}}\right) cos\theta' - H \right]}{\left[\left((1 + \frac{d_\mathrm{c}}{d_\mathrm{b}}) cos\theta' - H \right)^2 + \left((1 + \frac{d_\mathrm{c}}{d_\mathrm{b}}) sin\theta' \right)^2 \right]^{3/2}} d\theta' dH \tag{4.4}$$

where the angles θ_1 and θ_2 are the angles of intersection between the two overlapping circles described earlier. The nonequilibrium potential along the leading front is plotted in Fig. 5 of the main text.

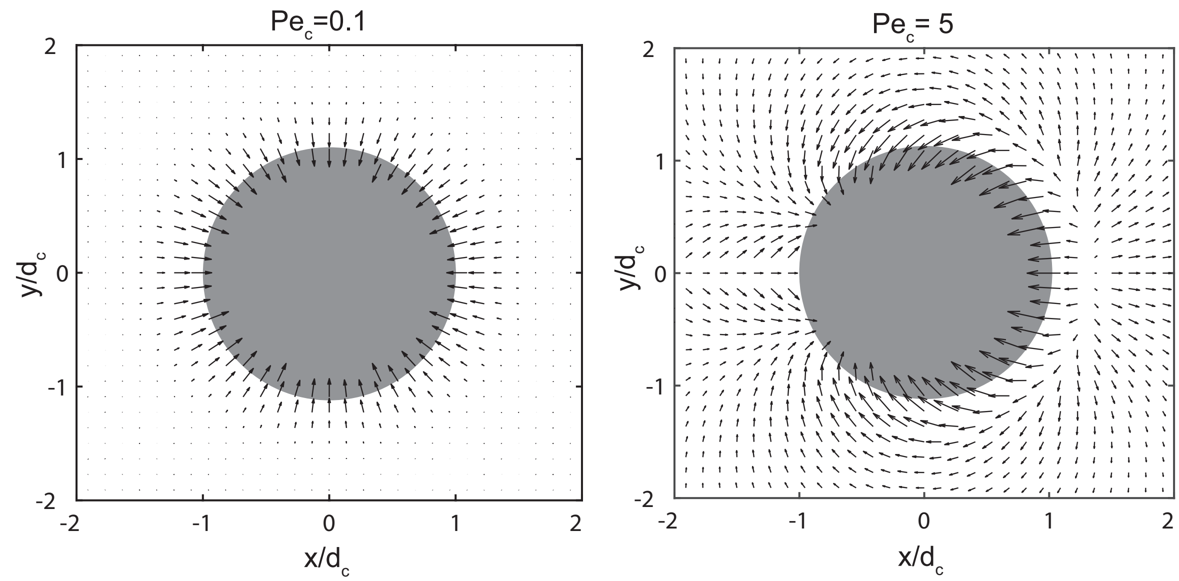

Figure 1 Vector plot showing theoretical calculations for the effective force field on the quiescent colloid in units of $k_B T/d_b$ for two different probe driving strengths: $\mathrm{Pe_c} = 0.1$ (left), and $\mathrm{Pe_c} = 5$ (right). The diffusivity ratio is $\alpha = 5$ and the shaded area $|r| < \mathrm{d_c}$ represents the excluded volume due to the hard-sphere colloid-colloid interaction.

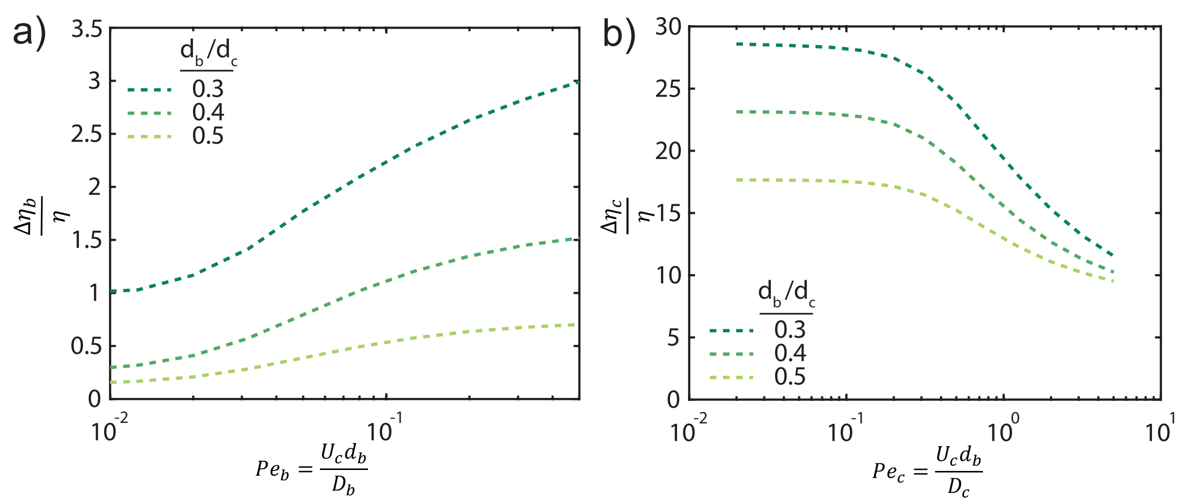

Figure 2 Microviscosity increments decrease for increasing depletant sizes. The depletant (a) and colloid (b) contributions to the microviscosity are shown for three different depletant-colloid size ratios.