Many-body Depletion Forces of Colloids in a Polydisperse Polymer Dispersant in the Long-chain Limit

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Supplemental Material

Derivation of the Many-Body Depletion Interaction for Large \( R_g \)

Eq.(8) (in the main text) with the specified boundary conditions is analogous to an electrostatic problem in the presence of a screening electrolyte (with a Debye length equal to \( R_g \)) and can be solved using standard Green’s function methods,\(^1\)

\[
\hat{g}(r_i, r_j) = 1 + \oint_{S_i} d\hat{s}_i G_0(|r_i - R_{is}\hat{s}_i|)\Lambda_i(\hat{s}_i) + \sum_{j \neq i} \oint_{S_j} d\hat{s}_j G_0(|r_i - R_{ij}| - R_{is}\hat{s}_j)\Lambda_j(\hat{s}_j)
\]

(S1)

where, \( r_i \) is the vector with origin at the \( i^{th} \) sphere, \( \hat{s}_j \) is the unit vector centered at the \( j^{th} \) sphere, which is integrated over all orientations and \( R_{ij} \) is the vector pointing from sphere \( i \) to sphere \( j \). \( G_0(r) \) is a Green’s function for the Helmholtz equation in free space

\[
\nabla^2 G_0(|r - r'|) - \lambda^2 G_0(|r - r'|) = \delta(r - r')
\]

(S2)

where \( \lambda = 1/R_g \) and

\[
\hat{G}_0(r) = \exp(-\lambda r)/4\pi\lambda r
\]

(S3)

which propagates chain density fluctuations in the fluid with the expected correlation length of \( R_g \). The surface “polarizations”, \( A_i \), describe the effect of the fixed spheres on the fluid, and are determined self-consistently so as to satisfy Eq.(9). Using the following expansions in spherical harmonics, \( Y^l_m(\hat{r}) \),

\[
\hat{g}(r) = \sum_{l = 0}^{\infty} \sum_{m = -l}^{l} \hat{g}^l_m(r)Y^l_m(\hat{r})
\]

(S4)
\[ \Lambda_i(s) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \Lambda_{lm}^l(r) Y_m^l(\hat{r}) \]  

(S5)

we can substitute into Eq.(S1) to obtain the following

\[ \hat{g}_m^l(r_i) = \sqrt{4\pi} \delta_0^l + \Gamma_{lm}(i) k_l(\lambda r_i) + i_l(\lambda r_i) \sum_{j \neq i}^N \sum_{l'}^l \sum_{m=-l'}^{l'} G_{lm,l'm}(\lambda R_{ij}) \Gamma_{l'm}(j) \]  

(S6a)

where

\[ \Gamma_{lm}(x) = \lambda \Lambda_m^l(x) i_l(\lambda R) \]  

(S6b)

\[ G_{lm,l'm}(\lambda R) = \sum_{LM} k_l(\lambda R) Q_{ll} C(lI0,000) C(l'l'M,000) Y_{l'M}(\hat{R}) \]  

(S6c)

\[ \delta_0^l \text{ is the Kronecker delta function, } C(l'l_1 l_2, m_1 m_2 m) \text{ is a Clebsch–Gordan coefficient,} \]

\[ Q_{l_1 l_2} = (-1)^{l_2} \sqrt{4\pi} \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{2l + 1} \right]^\frac{1}{2} \]  

(S6d)

and \( k_l(x) \) and \( i_l(x) \) are the modified spherical Bessel functions of the first and second kind respectively. Eqs (S6 a-d) were obtained using 1- and 2-centre expansions for the Yukawa function.\(^1,2\)

For large \( R_g \) we make the approximation that all but \( l = 0 \) terms can be set to zero. As we discuss later, this follows from the fact that \( \Gamma_0^0(r) \sim R_g^{-r} \) and correlations become exceptionally long-ranged making the surface polarizations less sensitive to the specific configurations of the spheres in the local environment. As a consequence, the surface polarization is slowly varying over the surface of a particle. Thus, we make a spherical approximation to obtain,\(^2\)

\[ \hat{g}_0^0(r_i) = \sqrt{4\pi} + \Gamma_0^0(i) k_0(\lambda r_i) + i_0(\lambda r_i) \sum_{j \neq i}^N k_0(\lambda R_{ij}) \Gamma_0^0(j) \]  

(S7)

Furthermore, given that the local environment about each sphere becomes relatively insensitive to the specific configuration of the surrounding spheres within the distance \( R_g \), the surface polarizations \( \Gamma_0^0(i) \) (for typical particle configurations) are only expected to vary on a length scale of \( R_g \) which allows us to make the following local approximation,\(^2\)
\[ \hat{g}_0^0(r_i) = \sqrt{4\pi} + \Gamma_{00}(i) k_0(\lambda r_i) + \Gamma_{00}(i) i_0(\lambda r_i) \sum_{j \neq i}^N k_0(\lambda R_{ij}) \]  

(S8)

Eq.(S8) can be solved at the sphere surfaces, using the boundary condition, Eq.(9) in the main text to give,

\[ \Gamma_{00}(i) = -\sqrt{4\pi} \left( k_0(\sigma) + i_0(\sigma) \sum_{j \neq i}^N k_0(\lambda R_{ij}) \right)^{-1} \]  

(S9)

where we have defined \( \sigma = \lambda R_S \) and \( k_0(x) = \exp^{\imath x} / x \).

Using Eq.(5) in the main text we can re-express the volume integral in Eq.(6) in terms of \( \nabla^2 \hat{g}(r; \Gamma) \) and convert this to a surface integral of \( \nabla \hat{g}(r; \Gamma) \) at each particle surface. Assuming only spherical (\( l = 0 \)) terms are non-zero, the radial derivative of \( \hat{g}_0^0(r_i) \) at the sphere surfaces can be obtained from Eq.(S8). Finally using Eq.(S9) we obtain the following (large \( R_g \)) form for the total POMF, which is equivalent to Eqs.(7-9).

\[ \omega(\Gamma) = N \omega^{(1)} - 4\pi R^3 g \Phi_{\text{chain}} \sum_{i=1}^N \frac{\sigma^2 e^{2\alpha} \sum_{j \neq i}^N k_0(\lambda R_{ij})}{1 + \frac{(e^{2\alpha} - 1)}{2} \sum_{k \neq i}^N k_0(\lambda R_{ik})} \]  

(S10)

where the 1-body insertion term is

\[ \beta \omega^{(1)} = 4\pi R^3 g \Phi_{\text{chain}} \left\{ \sigma + \sigma^2 + \frac{\sigma^3}{3} \right\} \]  

(S11)

The second term in Eq.(S10) is the total many-body contribution to the depletion interaction.

The so-called spherical and local approximations leading to Eq.(S9) and hence Eq.(S10) can be justified, by showing that the effective Hamiltonian Eq.(S10) between the particles lead to self-consistent solutions for \( \Gamma_{00}(i) \), as given by Eq.(S9). To do this we rewrite the many-body term after subtracting the 1-body contribution in Eq.(S9),

\[ -4\pi R^2 g R_S \Phi_{\text{chain}} \sum_{i=1}^N \sum_{j \neq i}^N k_0(\lambda R_{ij}) \left[ \frac{R^3 g}{e^{-2\alpha} / \sigma + \frac{1 - e^{-2\alpha}}{2\sigma}} \sum_{k \neq i}^N k_0(\lambda R_{ik}) \right] \]  

(S12)

where
\[ k_0(\lambda R) = R_{g}^{-3}k_0(\lambda R) \]  

(S13)

We shall assume that bulk conditions give a fixed value for \( R_{g}^2 \Phi_{\text{chain}} \) for all \( R_g \). The function \( k_0(\lambda R) \) has the form of a weak long-ranged Kac pair potential.\(^3\) A system that interacts via such a potential (in addition to a hard sphere interaction) is known to have a mean-field generalized van der Waals form in the limit where the range of the potential (in our case \( R \)) becomes infinite.\(^4-7\) We conjecture that the particles interacting via the many-body potential Eq.(S12) behave similarly to one with pair potential, Eq.(S13). This is because the term in square brackets in Eq.(S12) will remain finite as \( R_g \) grows.

For a system with a pair potential given by Eq.(S13) at large \( R_g \), sums of the type

\[ \sum_{k \neq i}^N k_0(\lambda R_{ik}) \]

can be replaced by their mean-field form (for particle configurations that contribute significantly to the partition function). That is,

\[ \sum_{k \neq i}^N k_0(\lambda R_{ik}) \approx 4\pi \rho_S \int_{2R_S}^{\infty} dR R^2 k_0(\lambda R) = 4\pi \rho_S e^{-2\sigma}(1 + 2\sigma) \]  

(S14)

Considering Eq.(S12) we find that replacing the sum in the denominator with the RHS of Eq.(S14) means that the term in square brackets approaches a finite constant, in the limit \( R_g \to \infty \), and the Hamiltonian does indeed have a Kac form of the type shown in Eq.(S13). This is consistent with our initial conjecture that the many-body potential produces the same mean-field thermodynamics as the pair potential, Eq.(S13). While this is not a rigorous proof, but merely a plausibility argument, this hypothesis is strongly supported by the very good agreement between the mean-field theory and simulations using the complete many-body potential, as shown in the main text, see Figure 1(b).

The argument leading to Eq.(S14), means that the local approximation, which gives rise to Eq.(S9) provides an accurate self-consistent solution for the set of

\[ \{\Gamma_{00}(i) \ i = 1, N\} \]

for large \( R_g \), as all sums, \( k \neq i \), are approximately equal over a length scale of \( R_g \) for the important particle configurations. To show that no higher moments \( (l > 0) \) need be considered, we note that the contributions to the surface polarizations at particle \( i \), due to all other particles \( j \) is given by the second term on the RHS of Eq.(S1)

\[ \sum_{j \neq i}^N \oint_{\Sigma_j} d\hat{s}_j G_0(|r_i - R_{ij} - R_S \hat{s}_j|) \Lambda_j(\hat{s}_j) \approx \Lambda_{00}(i) \sum_{j \neq i}^N k_0(\lambda |r_i - R_{ij}|) / 4\pi \]  

(S15)

where the RHS of Eq.(S15) is the contribution due to monopole terms and the local approximation has been used, also recall \( \Gamma_{00}(x) = \lambda \Lambda_{00}(x) i_0(\lambda R_s) \). In the limit of large \( R_s \), our previous arguments imply that the sum on the RHS is essentially independent of almost all configurations of importance and therefore is constant over the surface of the
sphere at $i$. This implies the asymmetric contributions generated by the monopole terms are small and all $\Gamma_{lm}(x)$ ($l>0$) can be set to zero.

References