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]

$$\hat{g}(r_i;\Gamma) = 1 + \oint_{S_i} d\hat{s}_i G_o(|r_i - R_S \hat{s}_i|)\Lambda_i(\hat{s}_i) + \sum_{j \neq i}^{N} \oint_{S_j} d\hat{s}_j G_o(|r_i - R_{ij} - R_S \hat{s}_j|)\Lambda_j(\hat{s}_j) \tag{S1}$$

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 $\boldsymbol{R}_{ij}$ 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

$$\nabla^2 \hat{G}_0(|\mathbf{r} - \mathbf{r}'|) - \lambda^2 \hat{G}_0(|\mathbf{r} - \mathbf{r}'|) = \delta(\mathbf{r} - \mathbf{r}') \tag{S2}$$

where $\lambda = 1/R_g$ and

$$\hat{G}_0(\boldsymbol{r}) = exp(-\lambda r)/4\pi\lambda r \tag{S3}$$

which propagates chain density fluctuations in the fluid with the expected correlation length of R_g. The surface "polarizations", Λ_j, 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, $Y^l_m(\hat{r})$,

$$\hat{g}(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \hat{g}^l_m(r) Y^l_m(\hat{r}) \tag{S4}$$

$$\Lambda_i(s) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \Lambda_{im}^{l}(r) Y_m^l(\hat{r}) \tag{S5}$$

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

$$\hat{g}_m^l(r_i) = \sqrt{4\pi}\delta_0^l + \Gamma_{lm}(i)k_l(\lambda r_i) + i_l(\lambda r_i)\sum_{j\neq i}^{N}\sum_{l'}\sum_{m'=-l'}^{l'} G_{lm,l'm'}(\lambda R_{ij})\Gamma_{l'm'}(j) \tag{S6a}$$

where

$$\Gamma_{lm}(x) = \lambda\Lambda_m^l(x)i_l(\lambda R_S) \tag{S6b}$$

$$G_{lm,l'm'}(\lambda R) = \sum_{LM} k_L(\lambda R)\, Q_{ll'L}C(ll'L,000)C(ll'L,mm'M)Y_M^L(\hat{R}) \tag{S6c}$$

δ_0^l is the Kronecker delta function, $C(l_1l_2l, m_1m_2m)$ is a Clebsch–Gordan coefficient,

$$Q_{l_1l_2l} = (-1)^{l_2}\sqrt{4\pi}\left[\frac{(2l_1+1)(2l_2+1)}{2l+1}\right]^{\frac{1}{2}} \tag{S6d}$$

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 $\hat{G}_0(r)\sim R_g/r$ 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]

$$\hat{g}_0^0(r_i) = \sqrt{4\pi} + \Gamma_{00}(i)k_0(\lambda r_i) + i_0(\lambda r_i)\sum_{j\neq i}^{N} k_0(\lambda R_{ij})\Gamma_{00}(j) \tag{S7}$$

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 $\Gamma_{00}(i)$ (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]

$$\hat{g}_0^0(r_i) = \sqrt{4\pi} + \Gamma_{00}(i) k_0(\lambda r_i) + \Gamma_{00}(i)\, i_0(\lambda r_i) \sum_{j \neq i}^{N} k_0(\lambda R_{ij}) \tag{S8}$$

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

$$\Gamma_{00}(i) = -\sqrt{4\pi}\left(k_0(\sigma) + i_0(\sigma) \sum_{j \neq i}^{N} k_0(\lambda R_{ij}) \right)^{-1} \tag{S9}$$

where we have defined $\sigma = \lambda R_S$ and $k_0(x) = exp(-x)/x$.

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).

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

(S10)

where the 1-body insertion term is

$$\beta\omega^{(1)} = 4\pi R_g^3 \Phi_{chain} \left\{ \sigma + \sigma^2 + \sigma^3/3 \right\} \tag{S11}$$

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),

$$-4\pi R_g^2 R_S \Phi_{chain} \sum_{i=1}^{N} \sum_{j \neq i}^{N} k_0(\lambda R_{ij}) \left[\frac{R_g^3}{e^{-2\sigma}/\sigma + \frac{(1 - e^{-2\sigma})}{2\sigma} R_g^3 \sum_{k \neq i}^{N} k_0(\lambda R_{ik})} \right] \tag{S12}$$

where

$\tilde{k}_0(\lambda R) = R_g^{-3} k_0(\lambda R)$ (S13)

We shall assume that bulk conditions give a fixed value for $R_g^2 \Phi_{chain}$ for all R_g. The function $\tilde{k}_0(\lambda R)$ 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_g) 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 $\sum_{k \neq i}^{N} \tilde{k}_0(\lambda R_{ik})$ can be replaced by their mean-field form (for particle configurations that contribute significantly to the partition function). That is,

$$\sum_{k \neq i}^{N} \tilde{k}_0(\lambda R_{ik}) \approx 4\pi\rho_S \int_{2R_S}^{\infty} dR R^2 \ \tilde{k}_0(\lambda R) = 4\pi\rho_S \, e^{-2\sigma}(1 + 2\sigma) \tag{S14}$$

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 $R_g \rightarrow \infty$, 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, $\sum_{k \neq i}^{N} \tilde{k}_0(\lambda R_{ik})$, 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)

$$\sum_{j \neq i}^{N} \oint_{S_j} d\hat{s}_j G_o\left(|r_i - R_{ij} - R_S \hat{s}_j|\right) \Lambda_j(\hat{s}_j) \approx \Lambda_0^0(i) \sum_{j \neq i}^{N} k_o\left(\lambda |r_i - R_{ij}|\right)/4\pi \tag{S15}$$

where the RHS of Eq.(S15) is the contribution due to monopole terms and the local approximation has been used, also recall $\Gamma_{00}(x) = \lambda \Lambda_0^0(x) i_0(\lambda R_S)$. In the limit of large R_g, 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.

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