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Exact Evaluation of the Depletion Force between Nanospheres in a Polydisperse Polymer Fluid under Θ Conditions

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Abstract

We use a continuum chain model and develop an analytical theory for the interaction between two spheres immersed in a fluid of polydisperse polymers under theta conditions. The theory is applied to both the cases where the spheres are either adsorbing or non-adsorbing spheres. Exact results are derived for the asymptotic behaviour of the depletion interaction for the case where the polymer fluid displays a Schulz-Flory molecular weight distribution. We show also that in the limit of large spheres (and large surface to surface separation) the Derjaguin approximation is valid. We compare our asymptotic expression with numerical solutions of an ideal equilibrium polymer fluid, consisting of discrete chains. Our asymptotic approximation accurately predicts long-range interactions between small spheres. For large spheres it predicts the interaction very well over most of the separation range. We also consider a single sphere immersed in the polymer fluid and show how our results can be generalized to treat polydisperse polymer fluids, where the polydispersity is described by a Schulz-Flory distribution.

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I. INTRODUCTION

Suspensions of spherical particles in polymer solutions are important systems to many industries, such as food, cosmetics and pharmaceuticals [1, 2]. This has spawned a great deal of experimental [3–7] and theoretical research [8–20].

When polymers are mixed with a dispersion of particles, they will profoundly influence particle interactions. In a classic experiment, Traube [21] added a water-soluble polymer to latex spheres to bring about their aggregation. This phenomenon is now understood to be due to depletion attractions [22, 23]. These forces occur when the density of polymer molecules is reduced in the region proximal to particle surfaces. If, on the other hand, polymer molecules are attracted to the particle surfaces they are able to bridge the space between particles, giving rise to so-called bridging attraction.

There have been a number of theoretical studies on depletion forces. These fall into two general classes: (i) *effective potential models* and (ii) *mixture models*. Effective potential models treat the particles as a single component fluid whose interactions are mediated by the underlying polymer solution. The latter is treated implicitly. For N particles at given fixed positions, the ensemble-averaged polymer configurations generate a general N -body free energy acting between the particles. This free energy can be formally partitioned into 1,2,... N -body contributions. The 1-body term corresponds to the excess chemical potential for insertion of a particle into the polymer solution at infinite dilution, while the 2-body interaction is obtained as the potential of mean-force (POMF) between two particles immersed in the polymer solution. Though it is conceptually appealing, any practical implementation of the effective potential approach must generally truncate the many-body series at the 2-body level, as the treatment of n -body interactions with $n \geq 3$ is generally too demanding numerically. Thus, pre-averaging over the polymer degrees of freedom is only useful when truncation at the 2-body interactions is a reasonable approximation. This is the case, in the so-called *colloidal* regime (large particle radius, R_s and small polymer radius of gyration R_g) as the occurrence of many-body collisions involving a polymer and more than two particles will be rare. However, in the case of *nanoparticles* wherein the polymer molecules are relatively larger than the particles, many-body forces are essential in order to obtain a proper thermodynamic description. This is also known at the *protein* regime.

In the *mixture models*, the polymer is treated *explicitly*, while the solvent remains implicit.

Unfortunately, the explicit treatment of all polymer degrees of freedom makes the problem numerically very demanding and further simplifications are generally needed. For example, Meijer *et al* [24] performed computer simulations wherein the polymer configurations were constrained to lie on a simple space-filling lattice. However, even in this case, the numerical generation of all polymer configurations is still extremely time consuming and very few studies using such models have appeared in the literature.

The Asakura-Oosawa (A-O) model [25, 26] simplifies the problem further by neglecting polymer configurations completely. In this case the particles and polymers are treated as spheres with non-additive radii. Assuming a Θ solvent, the polymer molecules are modelled as mutually penetrating spheres, with radius equal to R_g . On the other hand, the polymer spheres are unable to penetrate the particles. According to the A-O model, the range of the depletion interaction is determined by R_g and its strength depends on the osmotic pressure of the polymers. The A-O model has been widely studied by researchers in the field. For example, it is the basis of the free volume theory [27], which has been used to investigate the phase behaviour of polymer colloid mixtures with good success, when compared with simulations and experiment [7, 24, 28]. It has also been generalized to non- Θ solvents so as to account for polymer interactions [29, 30].

The A-O model relies on the assumption that the average volume traced out by polymer molecules within the particle matrix is approximately spherical and that the free energy cost for distortion away from a spherical shape is large. These assumptions may become difficult to justify in the nanoparticle regime. That is, the A-O model is expected to perform poorly when the ratio R_g/R_s is large. Here, polymer molecules will be significantly distorted from a spherical shape as they penetrate the particle matrix. By ignoring this effect, the A-O model is expected to predict a too strong depletion attraction between small spheres.

In recent work, we revisited the effective potential approach for a model of hard sphere particles and fully flexible ideal chains [31]. From the point of view of mathematical analysis, it was an advantage to treat a system of *polydisperse* polymers with a molecular weight dispersion described by the well-known Schulz-Flory distribution [32]. Serendipitously, a model that incorporates polydispersity in the polymer molecular weight is also more relevant to experimental conditions. Using this model, we are able to obtain an expression for the POMF between a pair of particles as an infinite multi-pole expansion, wherein the coefficients are conveniently obtained analytically. However, as described above, the POMF

alone is not sufficient for the description of nanoparticle dispersions, as the truncation the many-body series at the pair level becomes inaccurate. In order to overcome this problem, we have suggested a so-called "spherical approximation". The consequence of this approximation is that only monopole terms are required to describe many-body forces, leading to an enormous simplification of the resulting expression for the free energy [33, 34]. The spherical approximation can be physically described as follows. If N (spherical) particles are fixed in a typical configuration within the polymer solution, then the average density of monomers, *close* to the surface of any chosen particle, is approximately spherically symmetric about that particle's center. It is based on the idea that the local environment experienced by any one particle, in a sea of many, can reasonably be assumed to be spherically symmetric. That is, when many particles are present, the monopole contribution dominates the free energy, as the higher-order contributions will tend to cancel. This approximation is more plausible at high or moderate particle densities, but is less so when the density is small. At low density, particle configurations will likely be dominated by 2-particle clustering. Such asymmetric configurations could then lead to failure of the spherical approximation.

In this paper we will calculate the POMF between two particles immersed in a polydispersed polymer solution under Θ conditions. This is useful for two reasons. Firstly, this calculation has not been presented before, as our previous work reported only the asymptotic behaviour of the POMF. Hence, our results will provide an accurate representation of the 2-body interaction, which will be useful for describing colloidal dispersions. Secondly, the study of two particles allows us to explore the validity of the spherical approximation, especially in the regime of nanoparticles, wherein it provides a crucial simplification for the full many-body description. The 2-body system we describe here is expected to provide the strongest test of the spherical approximation. Despite the fact that much of the above discussion concerns depletion forces, our general derivations will consider both depleting and adsorbing particle surfaces.

The paper is arranged as follows. In the next section we will describe the general theory for two particles immersed in an ideal polymer fluid with a bulk molecular weight dispersion as given by the Schulz-Flory distribution. For completeness, we will also describe the many-body generalization, as presented in earlier work. We shall then provide the solution of the resultant equations for the POMF, using a multipole (or ℓ -pole) expansion of the polymer distribution. Analytical results are obtained for the cases $\ell = 0, 1$. More accurate solutions

are obtained for $\ell \leq L$, with large L and these are compared with the analytical results. We conclude with a discussion and some final comments.

II. THEORY

We consider two spherical particles (labelled A and B) immersed in a polymer solution under Θ conditions. The radius of sphere α is R_α and their centers are fixed at a separation R . We assume that the polymer molecules can be treated as ideal flexible chains which will sample their full configuration space, as allowed by the excluding spheres. Those configurations are described by the end-end segment distribution function, $G(\mathbf{r}, \mathbf{r}'; s)$, which denotes the joint probability that a chain segment of length s has ends at \mathbf{r} and \mathbf{r}' . This distribution satisfies the following "diffusion" equation,

$$\frac{\partial G(\mathbf{r}, \mathbf{r}'; s)}{\partial s} = \frac{\sigma^2}{6} \nabla^2 G(\mathbf{r}, \mathbf{r}'; s) - \psi(\mathbf{r}) G(\mathbf{r}, \mathbf{r}'; s) \quad (1)$$

with the initial boundary condition

$$G(\mathbf{r}, \mathbf{r}'; 0) = \delta(\mathbf{r} - \mathbf{r}') \quad (2)$$

Here, σ , is the Kuhn length and $\psi(\mathbf{r})$ is the external field acting on monomers. As we are dealing with a Θ solvent, we ignore the interactions between monomers and express $\psi(\mathbf{r})$ as a sum of spherically symmetric potentials centered on each particle. We assume these are short-ranged on the length-scale of the polymers. The affect of the spheres can then be described by applying the following homogeneous boundary condition at their surfaces,

$$\frac{1}{G} \nabla_{\mathbf{r}} G(\mathbf{r}, \mathbf{r}'; s) \cdot \hat{\mathbf{n}} = -\epsilon \quad \forall \mathbf{r} \in S \quad (3)$$

where $S = S_A \cup S_B$ is the union of surfaces of the two non-overlapping spheres. The quantity ϵ is a measure of the adsorption energy between polymers and the spheres and $\hat{\mathbf{n}}$ is a unit vector pointing outward and acting normal to the surfaces of the spheres.

A. Polydisperse Polymers

Solving Eq.s(1)-(3) is facilitated by considering the more general problem of a polydisperse polymer fluid where the molecular weight distribution can be described by the class

of Schulz-Flory (S-F) polydispersities [31]. These are described by the following normalized probability distributions,

$$F^{(n)}(\kappa, s) = \frac{\kappa^{n+1}}{\Gamma(n+1)} \frac{s^n}{\bar{s}^{n+1}} \exp(-\kappa s/\bar{s}) \quad (4)$$

Here s is the degree of polymerization and, $\Gamma(x)$, is the gamma function. In Eq.(4), we have also introduced the independent variable, κ . When $\kappa = n + 1$, then \bar{s} is the average polymer length. For the polydisperse fluid, $G(\mathbf{r}, \mathbf{r}'; s)$ is averaged over the molecular weight distribution to give $\hat{G}(\mathbf{r}, \mathbf{r}'; \kappa)$. For the case $n=0$, *equilibrium* polymers, we obtain

$$\hat{G}(\mathbf{r}, \mathbf{r}'; \kappa) = \int_0^\infty ds \frac{\kappa}{\bar{s}} \exp(-\kappa s/\bar{s}) G(\mathbf{r}, \mathbf{r}'; s) \quad (5)$$

Averaging both sides of Eq. (1) and using the boundary condition, Eq. (2), we get,

$$\frac{R_g^2}{\kappa} \nabla_{\mathbf{r}}^2 \hat{G}(\mathbf{r}, \mathbf{r}') - \hat{G}(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}') \quad (6)$$

where $R_g^2 = \bar{s}\sigma^2/6$ is the *average* square radius of gyration. Integrating one polymer end over the space external to the spheres (denoted as V') gives the following end-distribution function,

$$\hat{g}(\mathbf{r}) = \int_{V'} d\mathbf{r}' \hat{G}(\mathbf{r}, \mathbf{r}') \quad (7)$$

where $\hat{g}(\mathbf{r})$ is normalized to unity in the bulk (far from the spheres). The corresponding differential equation for $\hat{g}(\mathbf{r})$, ($\mathbf{r} \in V'$) is given by,

$$\nabla^2 \hat{g}(\mathbf{r}) - \lambda^2 \hat{g}(\mathbf{r}) + \lambda^2 = 0 \quad (8)$$

where $\lambda^2 = \kappa/R_g^2$. Note that the boundary conditions at the surfaces of the spheres are easily obtained from Eq.(3),

$$\frac{1}{\hat{g}} \nabla \hat{g}(\mathbf{r}) \cdot \hat{\mathbf{n}} = -\epsilon \quad \forall \mathbf{r} \in S \quad (9)$$

Perfectly depleting spheres correspond to $\epsilon \rightarrow -\infty$ and is characterized by Dirichlet boundary conditions,

$$\hat{g}(\mathbf{r}) = 0, \quad \forall \mathbf{r} \in S \quad (10)$$

Furthermore, we have that $\hat{g}(\mathbf{r}) \rightarrow 1$ far from the spheres. It is useful to introduce the Green's function for the associated Helmholtz equation in free space, [35]

$$\nabla_{\mathbf{r}}^2 G_0(|\mathbf{r} - \mathbf{r}'|) - \lambda^2 G_0(|\mathbf{r} - \mathbf{r}'|) = -\delta(\mathbf{r} - \mathbf{r}') \quad (11)$$

Given the bulk boundary conditions for $\hat{g}(\mathbf{r})$, we seek that $G_0(r) \rightarrow 0$ as $r \rightarrow \infty$. The required solution is given by,

$$G_0(r) = \frac{\exp(-\lambda r)}{4\pi r} \quad (12)$$

The solution to Eq.(8) can then be formally expressed as,

$$\hat{g}(\mathbf{r}) = \lambda^2 \int_V d\mathbf{r}' G_0(|\mathbf{r} - \mathbf{r}'|) + \oint_S d\mathbf{s} G_0(|\mathbf{r} - \mathbf{s}|) \Lambda(\mathbf{s}) \quad (13)$$

The function $\Lambda(\mathbf{s})$ provides multipole source terms at each of the the surfaces and is determined by the boundary condition Eq.(10). The first integral in Eq.(13) is over all space and is equal to unity. The second integral is over the surfaces of the two spheres. Thus, we obtain

$$\hat{g}(\mathbf{r}_A) = 1 + \oint_{S_A} d\hat{\mathbf{s}} G_0(|\mathbf{r}_A - \mathbf{s}|) \Lambda_A(\hat{\mathbf{s}}) + \oint_{S_B} d\hat{\mathbf{s}} G_0(|\mathbf{r}_A - \mathbf{s}|) \Lambda_B(\hat{\mathbf{s}}_j) \quad (14)$$

where the origin is chosen to be at the center of sphere A. We expand $\hat{g}(\mathbf{r})$ in spherical harmonics,

$$\hat{g}(\mathbf{r}_A) \approx \sum_{l=0}^L \sum_{m=-l}^l \hat{g}_m^l(r_A) Y_m^l(\hat{\mathbf{r}}_A) \quad (15)$$

where $\hat{\mathbf{r}}$ denotes the angular coordinates (θ, ϕ) of the vector \mathbf{r} with respect to the frame at sphere A.

The spherical harmonic functions are defined for $m \geq 0$ [36],

$$Y_m^l(\theta, \phi) = (-1)^m \sqrt{\left(\frac{2l+1}{4\pi}\right)} \sqrt{\left(\frac{l-m}{l+m}\right)} P_m^l(\cos\theta) e^{im\phi} \quad (16)$$

where $P_m^l(\cos\theta)$ is an associated Legendre polynomial, and $i = \sqrt{-1}$. For $m < 0$, we use the complex conjugate form,

$$Y_{\underline{m}}^l(\theta, \phi) = (-1)^m Y_m^l(\theta, \phi)^* \quad (17)$$

where we have used the notation $\underline{m} = -m$. The expansion, Eq.(15), becomes exact in the limit, $l_m \rightarrow \infty$, but in any practical calculation l_m will be finite. It is convenient to place the z-axis along the line joining the sphere centers. The problem becomes cylindrically symmetric, which allows us to set $m = 0$ in Eq.(15). A similar expansion can be made about the sphere B. The surface multipoles can also be expanded as,

$$\begin{aligned} \Lambda_A(\mathbf{s}) &\approx \sum_{l=0}^L \Lambda_0^l(A) Y_0^l(\hat{\mathbf{s}}) \\ \Lambda_B(\mathbf{s}) &\approx \sum_{l=0}^{L'} \Lambda_0^l(B) Y_0^l(\hat{\mathbf{s}}) \end{aligned} \quad (18)$$

where \mathbf{s} is a vector from the center to the surface of the sphere (A or B) and we note that in general the upper limit in the sums may be different for sphere A and B. For identical spheres we have reflection symmetry, $\Lambda(B)_0^l = (-1)^l \Lambda(A)_0^l$ and, in this case, we would choose $L = L'$. In order to obtain an expression for the first integral on the RHS of Eq.(14) we use the well-known 1-center expansion of the Green's function, G_0 about the sphere A.

$$G_0(|\mathbf{r} - \mathbf{r}'|) = \lambda \sum_{l=0}^{\infty} k_l(\lambda r_>) i_l(\lambda r_<) \sum_{m=-l}^l Y_m^l(\hat{\mathbf{r}}_>) Y_m^l(\hat{\mathbf{r}}_<)^* \quad (19)$$

where $\mathbf{r}_<$ and $\mathbf{r}_>$ are the lesser and greater respectively of \mathbf{r} and \mathbf{r}' . The modified spherical Bessel functions are defined as [37],

$$\begin{aligned} i_l(x) &= \sqrt{\frac{\pi}{2x}} I_{l+1/2}(x) \\ k_l(x) &= \sqrt{\frac{\pi}{2x}} K_{l+1/2}(x) \end{aligned} \quad (20)$$

where $I_\nu(x)$ and $K_\nu(x)$ are the modified Bessel functions of the first and second kind respectively. Evaluation of the second integral on the RHS of Eq.(14) uses a 2-center expansion for G_0 about both spheres, which we recently derived [31]

B. Two-center expansion for $G_0(|\mathbf{r} - \mathbf{r}'|)$

The 2-center expansion for the free space Green's function $G_0(|\mathbf{r} - \mathbf{r}'|)$, around the centers of the two spheres is obtained using the following decomposition,

$$\mathbf{r} - \mathbf{r}' = \mathbf{r} - \mathbf{r}'' - \mathbf{R} \quad (21)$$

where \mathbf{R} is the vector from sphere A to sphere B and \mathbf{r}'' , is the vector between the center of sphere B and the vector \mathbf{r}' . Assuming $|\mathbf{R}| \geq |\mathbf{r} - \mathbf{r}''|$, which will be true in our application, we obtain

$$\begin{aligned} G_0(|\mathbf{r} - \mathbf{r}'' - \mathbf{R}|) &= \lambda \sum_{l_1, m_1} \sum_{l_2, m_2} \sum_{l, m} k_l(\lambda R) i_{l_1}(\lambda r) i_{l_2}(\lambda r'') \\ &\quad \times Q_{l_1 l_2 l} C(l_1 l_2 l; 000) C(l_1 l_2 l; m_1 m_2 m) \\ &\quad \times Y_m^l(\hat{\mathbf{R}}) Y_{m_1}^{l_1}(\hat{\mathbf{r}})^* Y_{m_2}^{l_2}(\hat{\mathbf{r}}'')^* \end{aligned} \quad (22)$$

where $C(l_1 l_2 l; m_1 m_2 m)$ is a Clebsch-Gordan coefficient and

$$Q_{l_1 l_2 l} = (-1)^{l_2} (4\pi)^{\frac{1}{2}} \left[\frac{(2l_1 + 1)(2l_2 + 1)}{(2l + 1)} \right]^{\frac{1}{2}} \quad (23)$$

We note that

$$\sum_{m_1, m_2, m} C(l_1 l_2 l; m_1 m_2 m) Y_m^l(\hat{\mathbf{R}}) Y_{m_1}^{l_1}(\hat{\mathbf{r}})^* Y_{m_2}^{l_2}(\hat{\mathbf{r}}'')^* \quad (24)$$

are rotational invariants. The appearance of these combinations are a consequence of rotational symmetry of $G_0(r)$. As before, we choose the z -axis to coincide with the $\hat{\mathbf{R}}$ direction to obtain the following simplification,

$$\begin{aligned} G_0(|\mathbf{r} - \mathbf{r}'' - \mathbf{R}|) &= \lambda \sum_{l_1, l_2, l} \sum_m k_l(\lambda R) i_{l_1}(\lambda r) i_{l_2}(\lambda r'') \\ &\times (-1)^{l_2} A_{l_1 l_2} C(l_1 l_2 l; 000) C(l_1 l_2 l; m \underline{m} 0) Y_m^{l_1}(\hat{\mathbf{r}}) Y_{\underline{m}}^{l_2}(\hat{\mathbf{r}}'') \end{aligned} \quad (25)$$

where, $A_{l_1 l_2} = [(2l_1 + 1)(2l_2 + 1)]^{\frac{1}{2}}$ and we have taken the complex conjugate of the RHS of Eq.(25).

Substituting these expansions for $G_0(|\mathbf{r} - \mathbf{r}'|)$ into the RHS of Eq.(14) and using the spherical harmonic expansions for the surface multipoles, gives the following expansion coefficients for the function $\hat{g}(\mathbf{r})$, about sphere A.

$$\hat{g}_0^l(r) = \sqrt{4\pi} \delta_0^l + \Gamma_l(A) k_l(\lambda r) + i_l(\lambda r) \sum_{l'} G_{l, l'}(\lambda R) \Gamma_{l'}^*(B) \quad (26)$$

where we have defined *renormalized* multipole field strengths,

$$\Gamma_l(X) = \lambda \Lambda_0^l(X) i_l(\lambda R_s) \quad (27)$$

with $\Gamma_l^*(X) = (-1)^l \Gamma_l(X)$, and

$$G_{l_1 l_2}(\lambda R) = A_{l_1 l_2} \Sigma_l k_l(\lambda R) C_{l_1 l_2 l; 000}^2 \quad (28)$$

Using Eq.(26) and the logarithmic boundary conditions at each surface,

$$\epsilon \hat{g} + \nabla \hat{g}(\mathbf{r}) \cdot \hat{\mathbf{n}} = 0 \quad \forall \mathbf{r} \in S \quad (29)$$

we are able to solve for the surface multipoles, $\Gamma_l(X)$. For example, we have at the surface of sphere A,

$$\Gamma_l(A) \mathcal{K}_l(\lambda R_A) + \mathcal{I}_l(\lambda R_A) \sum_{l'} G_{l, l'}(\lambda R) \Gamma_{l'}^*(B) = -\epsilon \sqrt{4\pi} \delta_0^l \quad (30)$$

$$\mathcal{K}_l(x) = \epsilon k_l(x) + \lambda k'_l(x) \quad (31)$$

and

$$\mathcal{I}_l(x) = \epsilon i_l(x) + \lambda i'_l(x) \quad (32)$$

The general equation is most conveniently written in matrix form as,

$$\begin{bmatrix} \mathbf{J}_A & \mathbf{G} \\ \mathbf{G}^T & \mathbf{J}_B \end{bmatrix} \times \begin{bmatrix} \Gamma_0(A) \\ \vdots \\ \Gamma_L(A) \\ \Gamma_0^*(B) \\ \vdots \\ \Gamma_{L'}^*(B) \end{bmatrix} = -\epsilon\sqrt{4\pi} \begin{bmatrix} 1/\mathcal{I}_0(\lambda R_A) \\ 0 \\ \vdots \\ 1/\mathcal{I}_0(\lambda R_B) \\ 0 \\ \vdots \end{bmatrix} \quad (33)$$

where the $(L+1) \times (L+1)$ submatrix \mathbf{J}_A is diagonal, with elements

$$\mathbf{J}_A = \begin{bmatrix} \frac{\mathcal{K}_0(\lambda R_A)}{\mathcal{I}_0(\lambda R_A)} & 0 & \dots & 0 \\ 0 & \frac{\mathcal{K}_1(\lambda R_A)}{\mathcal{I}_1(\lambda R_A)} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{\mathcal{K}_L(\lambda R_A)}{\mathcal{I}_L(\lambda R_A)} \end{bmatrix} \quad (34)$$

with a similar expression for the $(L'+1) \times (L'+1)$ submatrix \mathbf{J}_B . Furthermore, the expression for the for the $(L+1) \times (L'+1)$ submatrix \mathbf{G} is given by,

$$\mathbf{G} = \begin{bmatrix} G_{00} & \dots & G_{0L'} \\ \vdots & \ddots & \vdots \\ G_{L0} & \dots & G_{LL'} \end{bmatrix} \quad (35)$$

where the elements are given by Eq.(28). We shall denote the matrix on the LHS of Eq.(33) as $\mathcal{M} = \mathcal{J} + \mathcal{G}$, where \mathcal{J} is the diagonal matrix made up of the submatrices \mathbf{J}_A and \mathbf{J}_B , and \mathcal{G} is the residual component consisting of the \mathbf{G} submatrices. It is useful to note that the element of \mathcal{G} approach zero, as the distance between the spheres becomes large.

C. Polymer Free Energy

The expansion coefficient Γ_0 is (to within a constant), proportional to the polymer free energy. To see this, we note that the excess free energy of the polymer fluid in the presence

of the spheres (beyond the bulk value), is given by,

$$\beta\Delta\omega_{tot} = -\Phi_p \int_V d\mathbf{r} \{\hat{g}(\mathbf{r}) - 1\} \quad (36)$$

where $\beta = 1/k_B T$. Using the second order differential equation for $\hat{g}(\mathbf{r})$, Eq.(8), we can rewrite the free energy as,

$$\beta\Delta\omega_{tot} = -\frac{\Phi_p}{\lambda^2} \int_{V'} d\mathbf{r} \nabla^2 \hat{g}(\mathbf{r}) + \Phi_p \sum_{i=A,B} 4\pi R_s^3/3 \quad (37)$$

Gauss's Theorem allows us to reexpress the volume integrals in Eq.(37) in terms of surface integrals of $\nabla \hat{g}(\mathbf{r})$ at each sphere,

$$\int_{V'} d\mathbf{r} \nabla^2 \hat{g}(\mathbf{r}) = - \sum_{i=A,B} R_i^2 \int_{S_i} d\sigma \cdot \nabla \hat{g} \quad (38)$$

where S_i represents the surface of sphere i and σ is the unit surface vector, which points outward from the spherical center. From the boundary condition, Eq.(29), we finally obtain,

$$\int_{S_i} d\sigma \cdot \nabla \hat{g}(\mathbf{r}) = -\sqrt{4\pi} R_i^2 \epsilon \hat{g}_0^l(R_i) \quad (39)$$

where the spherically symmetric component of $\hat{g}(\mathbf{r})$ has been selected, by the integration over the spherical surface. This can be expressed as

$$\beta\Delta\omega_{tot} = -\Phi_p \frac{\sqrt{4\pi}\epsilon}{\lambda^2} \sum_{i=A,B} R_i^2 \hat{g}_0^l(R_i) + \Phi_p \sum_{i=1}^{N_s} 4\pi R_s^3/3 \quad (40)$$

Using Eq.(26) we obtain for the component of the gradient perpendicular to the surface of sphere A ,

$$\frac{\partial \hat{g}_0^l(r)}{\partial r} = \Gamma_l(A) \lambda k_l'(\lambda r) + \lambda i_l'(\lambda r) \sum_{l'} G_{l,l'}(\lambda R) \Gamma_{l'}^*(B) \quad (41)$$

Combining Eq.s (41) and (26) using the boundary condition Eq.(29), we obtain,

$$\mathcal{K}_l(\lambda R_A) \Gamma_l(A) + \mathcal{I}_l(\lambda R_A) \sum_{l'} G_{l,l'}(\lambda R) \Gamma_{l'}^*(B) = -\epsilon \sqrt{4\pi} \delta_0^l \quad (42)$$

Using the following relationship, easily derived from the properties of the modified spherical Bessel functions,

$$i_l(x) \mathcal{K}_l(x) = k_l(x) \mathcal{I}_l(x) - \frac{\lambda}{x^2} \quad (43)$$

we multiply Eq.(42) by $i_l(\lambda R_A)$ to obtain

$$\mathcal{I}_l(\lambda R_A) k_l(\lambda R_A) \Gamma_l(A) + \mathcal{I}_l(\lambda R_A) \sum_{l'} G_{l,l'}(\lambda R) \Gamma_{l'}^*(B) - \frac{\Gamma_l(A)}{\lambda R_A^2} = -i_l(\lambda R_A) \epsilon \sqrt{4\pi} \delta_0^l \quad (44)$$

which we reexpress as,

$$\mathcal{I}_l(\lambda R_A)\{g_0^l(R_A) - \sqrt{4\pi}\delta_0^l\} - \frac{\Gamma_l(A)}{\lambda R_A^2} = -i_l(\lambda R_A)\epsilon\sqrt{4\pi}\delta_0^l \quad (45)$$

and finally rearrange to obtain,

$$g_0^l(R_A) = \sqrt{4\pi}\delta_0^l \frac{\lambda i'_l(\lambda R_A)}{\mathcal{I}_l(\lambda R_A)} + \frac{\Gamma_l(A)}{\mathcal{I}_l(\lambda R_A)\lambda R_A^2} \quad (46)$$

Substituting back into Eq.(40), we obtain the following general expression for the free energy,

$$\frac{\beta\Delta\omega_{tot}}{4\pi\Phi_p^*} = -\kappa^{-3/2} \sum_{i=A,B} \left\{ \frac{\epsilon\sigma_i^2 i_1(\sigma_i)}{\mathcal{I}_0(\sigma_i)} + \frac{\epsilon\Gamma_0(i)}{\sqrt{4\pi}\mathcal{I}_0(\sigma_i)} - \frac{\sigma_i^3}{3} \right\} \quad (47)$$

where we have used the fact that $i'_0(x) = i_1(x)$ and defined $\sigma_i = \lambda R_i$ and $\Phi_p^* = \Phi_p R_g^3$.

$$\Gamma_0(A) = -\frac{\sqrt{4\pi}\epsilon}{\mathcal{I}_0(\sigma_A)} \mathcal{M}_{00}^{-1} \quad (48)$$

and

$$\Gamma_0(B) = -\frac{\sqrt{4\pi}\epsilon}{\mathcal{I}_0(\sigma_B)} \mathcal{M}_{L+1L+1}^{-1} \quad (49)$$

III. RESULTS

A. Analytical results for identical spheres in the protein limit

From here on, we shall assume identical ($A = B$) spheres. This notwithstanding, the analysis presented does not rely on this simplification. The problem simplifies, by noting that, $\Gamma_l(A) = \Gamma_l^*(B) = \Gamma_l$ and hence we are able to write,

$$[\mathbf{M}] \times \begin{bmatrix} \Gamma_0 \\ \vdots \\ \Gamma_L \end{bmatrix} = -\sqrt{4\pi}\epsilon \begin{bmatrix} 1/\mathcal{I}_0(\sigma) \\ 0 \\ \vdots \end{bmatrix} \quad (50)$$

where the reduced matrix $\mathbf{M}(=\mathbf{J} + \mathbf{G})$, has dimensions $(L+1) \times (L+1)$. $\sigma = \lambda R_S$, where R_S is the radius of both spheres and

$$\mathbf{J} = \begin{bmatrix} \frac{\mathcal{K}_0(\sigma)}{\mathcal{I}_0(\sigma)} & 0 & \dots & 0 \\ 0 & \frac{\mathcal{K}_1(\sigma)}{\mathcal{I}_1(\sigma)} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \frac{\mathcal{K}_L(\sigma)}{\mathcal{I}_L(\sigma)} \end{bmatrix} \quad (51)$$

Hence the exact solution to Eq.(50) is given by

$$\Gamma_0 = -\frac{\sqrt{4\pi\epsilon}}{\mathcal{I}_0(\sigma)}\mathbf{M}_{00}^{-1} \quad (52)$$

Closed analytic expressions can be obtained for \mathbf{M}_{00}^{-1} for finite L . However, they rapidly become more complex as L increases. However, in the protein limit ($R_S/R_g \rightarrow 0$) the solution is rather simple. Considering Eq.(30) and letting $\sigma_i \rightarrow 0$ we see that only the monopole ($l = 0$) term survives this process. Mathematically, this follows from the fact that $i_l(0) = 0$ for $l > 0$, and $i_0(0) = 1$. Physically, this is because the influence due to sphere B on the value of $\hat{g}(\mathbf{r})$ on the surface of sphere A is essentially constant. This is due to the relatively small size of the spheres compared with R_g and therefore, only monopole source terms are required to ensure surface boundary conditions. Hence we obtain,

$$\Gamma_0 = \frac{-\sqrt{4\pi\epsilon}}{\mathcal{K}_0(\sigma) + \mathcal{I}_0(\sigma)G_{00}(\lambda R)} \quad (53)$$

where G_{00} is,

$$G_{00}(x) = \frac{e^{-x}}{x} \quad (54)$$

Substituting this result into Eq.(47) and subtracting the 1-body contributions to the free energy, we get the following interaction free energy between the spheres,

$$\frac{\beta\Delta\omega_2^{(0)}}{4\pi\Phi_p^*} = -2\kappa^{-3/2} \frac{\epsilon^2 G_{00}(R)}{\mathcal{K}_0(\sigma)(\mathcal{K}_0(\sigma) + \mathcal{I}_0(\sigma)G_{00}(R))} \quad (55)$$

Explicit expression for the modified spherical Bessel functions are: $i_0(x) = \sinh(x)/x$, $k_0(x) = \exp(-x)/x$, $i'_0(x) = \{x\cosh(x) - \sinh(x)\}/x^2$ and $k'_0(x) = -\exp(-x)(x+1)/x^2$. Small σ expansion gives the following, $\mathcal{I}_0(\sigma) \sim \epsilon + \lambda\sigma/3$, and $\mathcal{K}_0(\sigma) \sim \epsilon/\sigma - \lambda/\sigma^2$ which leads to,

$$\frac{\beta\Delta\omega_2^{(0)}}{4\pi\Phi_p^*} \sim -2\kappa^{-3/2} \frac{\epsilon^2\sigma^4 G_{00}(R)}{(\epsilon\sigma - \lambda\sigma - \lambda)^2} \quad (56)$$

which, in explicit terms, is

$$\beta\Delta\omega_2^{(0)} \sim -8\pi\Phi_p^*(R_S/R_g)^2 \frac{\epsilon^{*2}}{(\epsilon^* - 1 - \sqrt{\kappa}R_S/R_g)^2} \frac{\exp(-\sqrt{\kappa}R/R_g)}{\kappa R/R_g} \quad (57)$$

where we have defined the dimensionless adsorption strength $\epsilon^* = \epsilon R_S$. For the case of *equilibrium* (or living) polymers we substitute $\kappa = 1$. For attractive spheres, $\epsilon > 0$, it is possible that the denominator term in the prefactor of Eq.(61) can become zero. This corresponds to a surface adsorption transition, which has been previously shown to occur

on planar surfaces in the presence of a polymer solution with a Schulz-Flory distribution of molecular weights [38]. The more monodispersed the solution becomes ($\kappa \rightarrow \infty$), the greater the adsorption strength required to achieve this transition. For monodispersed solutions of finite polymer length, an infinite adsorption is necessary. Interestingly, as the spheres become smaller in size, a larger adsorption is also required to achieve a similar result.

As we have shown in previous work [31], it is possible to obtain the corresponding free energies for higher-order Schulz-Flory distributions by using the following relation,

$$\begin{aligned}\Delta\omega_2^{(n)}(\kappa) &= \sum_{m=0}^n \frac{(-\kappa)^m}{m!} \frac{\partial^m}{\partial \kappa^m} \Delta\omega_2^{(0)} \\ &= \hat{L}_\kappa^{(n)} \Delta\omega_2^{(0)}\end{aligned}\quad (58)$$

where $\Delta\omega_2^{(n)}(\kappa)$ with $\kappa = n + 1$, is the interaction between two spheres in the presence of a polymer fluid with a Schulz-Flory distribution given by $F^{(n)}(\kappa, s)$ in Eq.(4). As, $n \rightarrow \infty$, the polymer becomes more monodisperse. Alternatively, from Eq.(5) it is straightforward to see that the interaction in the case of *monodispersed* polymers is given by the inverse Laplace transform of $\Delta\omega_2^{(0)}/\kappa$. That is, substituting the interaction free energy into Eq.(5), we have,

$$\kappa^{-1} \Delta\omega_2^{(0)} = \int_0^\infty dt e^{-\kappa t} \Delta\omega_2^{(\infty)}(st) \quad (59)$$

where $\Delta\omega_2^{(\infty)}(s)$ is the interaction between two spheres in a monodisperse polymer solution with polymer length s . Hence,

$$\Delta\omega_2^{(\infty)}(s) = \mathcal{L}^{-1}\{\kappa^{-1} \Delta\omega_2^{(0)}\}(t = 1) \quad (60)$$

where \mathcal{L}^{-1} denotes the inverse Laplace transform. For the case of perfectly depleting spheres, $\epsilon^* \rightarrow -\infty$, which gives,

$$\beta \Delta\omega_2^{(0)} \sim -8\pi \Phi_p^*(R_S/R_g)^2 \frac{\exp(-\sqrt{\kappa}R/R_g)}{\kappa R/R_g} \quad (61)$$

which upon substitution into Eq.(60) gives the known expression for the depletion interaction between small spheres (protein limit) in an ideal monodispersed polymer, first derived by Eisenriegler and coworkers [39],

$$\beta \Delta\omega_2^{(\infty)} \sim -\Phi_p^*(R_S/R_g)^2 \frac{32\pi}{R/R_g} i^2 \text{erfc}\left(\frac{R}{2R_g}\right) \quad (62)$$

where $\text{i}^2\text{erfc}(x)$ is the twice-iterated complementary error function [37]. On the other hand, for small spheres with finite ϵ , such that $|\epsilon^*|, \sqrt{\kappa}R_S/R_g \ll 1$, we obtain

$$\beta\Delta\omega_2^{(0)} \sim -8\pi\Phi_p^*(R_S/R_g)^2\epsilon^{*2}\frac{\exp(-\sqrt{\kappa}R/R_g)}{\kappa R/R_g} \quad (63)$$

When we consider the transition to more monodispersed polymer solutions, it is assumed that the spheres are small enough so that the condition, $\sqrt{\kappa}R_S/R_g \ll 1$, applies as κ increases. Thus, for finite ϵ , progression to the monodisperse case gives the following sequential limit (in the protein limit),

$$\beta\Delta\omega_2^{(\infty)} \sim -\Phi_p^*\epsilon^{*2}(R_S/R_g)^2\frac{32\pi}{R/R_g}\text{i}^2\text{erfc}\left(\frac{R}{2R_g}\right) \quad (64)$$

This results shows that the pair interaction for small spheres is symmetric about the non-adsorbing case ($\epsilon = 0$). As far as we are aware, this is the first time that this result has been reported.

Corrections to $\Delta\omega_2^{(0)}$, for larger spheres can be obtained by analytically inverting the matrix \mathbf{M} , which is convenient for low L . This is illustrated here for $L = 1$. In that case we obtain,

$$\mathbf{M} = \begin{bmatrix} G_{00}(R) + \mathcal{K}_0(\sigma)/\mathcal{I}_0(\sigma) & G_{01}(R) \\ G_{10}(R) & G_{11}(\lambda R) + \mathcal{K}_1(\sigma)/\mathcal{I}_1(\sigma) \end{bmatrix} \quad (65)$$

$$\mathbf{M}^{-1} = \frac{1}{\det(\mathbf{M})} \begin{bmatrix} G_{11}(R) + \mathcal{K}_1(\sigma)/\mathcal{I}_1(\sigma) & -G_{01}(R) \\ -G_{10}(R) & G_{00}(R) + \mathcal{K}_0(\sigma)/\mathcal{I}_0(\sigma) \end{bmatrix} \quad (66)$$

giving,

$$\Gamma_0 = -\sqrt{4\pi\epsilon}\frac{G_{11}(R) + \mathcal{K}_1(\sigma)/\mathcal{I}_1(\sigma)}{\mathcal{I}_0(\sigma)\det(\mathbf{M})} \quad (67)$$

Where $\det(\mathbf{M})$ is the determinant of \mathbf{M} . Also we have,

$$G_{01}(R) = \sqrt{3}\frac{e^{-\lambda R}(\lambda R + 1)}{(\lambda R)^2} \quad (68)$$

and $G_{10}(R) = G_{01}(R)$.

$$G_{11}(R) = \frac{(\lambda R)^2 e^{-\lambda R} + 2e^{-\lambda R}(\lambda R^2 + 3\lambda R + 3)}{(\lambda R)^3} \quad (69)$$

The expression for Γ_0 can be substituted back into Eq.(47) to obtain a higher order, analytic expression for the potential for the free energy,

$$\frac{\beta\Delta\omega_2^{(0)}}{4\pi\Phi_p^*} = -2\kappa^{-3/2}\epsilon^2\frac{G_{00}(R) + \Delta G(R)}{\mathcal{K}_0(\sigma)\{\mathcal{K}_0(\sigma) + \mathcal{I}_0(\sigma)(G_{00}(R) + \Delta G(R))\}} \quad (70)$$

where

$$\Delta G(R) = -\frac{G_{01}(R)^2}{G_{11}(R) + \mathcal{K}_1(\sigma)/\mathcal{I}_1(\sigma)} \quad (71)$$

While it is still possible to obtain analytic expressions for even larger L , they become cumbersome, so we chose to solve cases for $L > 1$ numerically.

B. Numerical Evaluations

Using ©Matlab 2007, we solved the case of two perfectly depleting spheres ($\epsilon \rightarrow -\infty$) with varying ratios $q = R_g/R_S$. The upper angular momentum was varied from $L = 2, \dots, 9$. The quantity Γ_0 was then obtained as a function of the separation between the spheres R . The variation of Γ_0 with respect to the number of spherical harmonics used was investigated for different q . The results for Γ_0 with varying L values are given in the figures below. As expected, in the protein regime, the surface multipoles can be approximated with small L values. In the colloidal regime, a larger L need to be used in order to get a reasonable value for the interaction free energy. The reason for this is the polymers in the colloidal regime explore more spatial variation around the two adjacent spheres than for the case of the protein regime. In the latter case, the distribution function $\hat{g}(\mathbf{r})$ is much less affected by the spherical surfaces, and the spherical harmonic expansion of $\hat{g}(\mathbf{r})$ can be truncated at a small L .

IV. CONCLUSION

The analysis carried out in earlier work on the interaction between spherical particles in an ideal polymer solution with a Schulz-Flory polydispersity has been generalized to the case of arbitrary adsorption strength. Analytical results have been obtained in the case of small particles (protein limit), which are consistent with earlier analytical work by Eisenriegler and coworkers. Furthermore, we have carried out a numerical evaluation of the POMF, which takes into account a more extensive multipole expansion. The interesting result that emerges is that a low order truncation of the multipole expansion becomes more accurate, as the particles are made smaller, relative to the average polymer radius of gyration. Indeed, for perfectly depleting spheres and $R_g/R_s > 1$ it appears that the monopole term is largely sufficient to provide an accurate representation of the POMF, even when the spheres are at contact. Furthermore, analytic corrections for the addition of dipolar terms ($\ell = 0, 1$) are easily derived in the framework of our analysis.

The two particle system we describe herein provides a stringent test of the spherical approximation that has been recently invoked by us to describe the many-body interaction in N-particle dispersions of depleting particles. We have shown that the $\ell = 0$ approximation embodied in that assumption is justified in the protein limit, which is precisely when many-body forces (beyond the POMF) are expected to be most important. Thus far the protein limit has been considered the most difficult one to treat theoretically, due to the ability of polymers to penetrate between particles. On the other hand, the colloidal limit can be easily dealt with using the pair (2-particle) approximation. Our results show that the effective potential approach for depletion forces can be *significantly simplified* in the protein regime. The general symmetry of repulsive and attractive particle surfaces also mean that this effective many-body potential approach to bridging interactions should also be possible.

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