

Note

An approximate method for calculating depletion and structural interactions between colloidal particles

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Abstract

An approximate method is evaluated for calculating the second virial coefficient in a dilute macromolecular solution bounded by two interfaces. The approximation is essentially the superposition of the coefficients calculated independently for each surface. To test this approach, the depletion interaction between two particles in a solution of nonadsorbing, spherical macromolecules is calculated in systems with either hard-wall or long-range electrostatic interactions. In all systems tested, the interparticle interaction energy calculated with the approximation is found to be in good agreement with that calculated using the exact approach (e.g., error less than 2% at the smallest separations). The primary advantage of this approximation is a significant reduction in the computation time required for calculating the depletion interaction, especially in charged systems. The paper also shows that the expressions for predicting the depletion interaction in purely hard-sphere systems can be used in dilute ionic systems, provided the appropriate effective macromolecule size is used. For the attractive depletion interaction, this effective size is determined by the range of the particle–macromolecule interaction (as opposed to the macromolecule–macromolecule interaction).

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1. Introduction

The depletion interaction between two colloidal particles in the presence of a nonadsorbing species (henceforth referred to as macromolecules) has received considerable attention over the past several years and a variety of computational approaches have been developed for producing this force (see Jenkins and Snowden [1]) for a good review). One of the relatively simplest, though approximate, approaches is the force balance model of Walz and Sharma [2]. Essentially, this model calculates the force exerted on a particle by summing the particle/macromolecule force over all macromolecules in solution (explained in greater detail in Section 2).

The Walz and Sharma model uses a virial expansion of the single particle distribution function to calculate the spatial distribution of macromolecules in solution. Because the

virial expansion is truncated after the second term, the model is valid only for relatively dilute solutions (i.e., effective macromolecule concentration of order 1%). One reason for its relative simplicity is that the model uses an approximate method for calculating the second virial coefficient for a macromolecule that is positioned so that it can interact simultaneously with two neighboring particles. Effectively, the approximation is a superposition of the virial coefficients calculated for each of the particle/macromolecule interactions independently. The objective of this work is to examine the validity of this approximation in systems having either simple hard-sphere or longer-range electrostatic interactions.

2. Theory

A detailed description of the Walz and Sharma model can be found elsewhere [2,3]. Here we present a basic overview. Consider two spherical particles, 1 and 2, of radius R immersed in an equilibrium solution of nonadsorbing spherical macromolecules of radius a and bulk number density ρ_b .

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The force exerted on particle 1, \mathbf{F}_1 , by the macromolecules can be calculated as

$$\mathbf{F}_1(\mathbf{r}_{12}) = - \int_{\mathbf{r}_1} \rho(\mathbf{r}_1, \mathbf{r}_2, \rho_b) \nabla_1 E_{m-p1}(\mathbf{r}_1, \mathbf{r}_2, \rho_b) d\mathbf{r}_1, \quad (1)$$

where \mathbf{r}_1 is the position of a macromolecule defined relative to the center of particle 1, \mathbf{r}_{12} is a vector pointing from the center of particle 1 to the center of particle 2, \mathbf{r}_2 is the position of a macromolecule relative to the center of particle 2 ($\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{r}_{12}$), $\rho(\mathbf{r}_1, \mathbf{r}_2, \rho_b)$ is the local density of macromolecules at position \mathbf{r}_1 , and $-\nabla_1 E_{m-p1}(\mathbf{r}_1, \mathbf{r}_2, \rho_b)$ is the mean force acting on a macromolecule located at position \mathbf{r}_1 with respect to the surface of particle 1.

Walz and Sharma calculated the density distribution of macromolecules at any position in the fluid using a second order virial expansion in bulk macromolecule number density of the form

$$\rho(\mathbf{r}_1, \mathbf{r}_2, \rho_b) = \rho_b \exp\left[-\frac{E_m(\mathbf{r}_1, \mathbf{r}_2, \rho_b)}{kT}\right] \times [1 + b_2(\mathbf{r}_1, \mathbf{r}_2, \rho_b)\rho_b], \quad (2)$$

where b_2 is the second order virial coefficient and $E_m(\mathbf{r}_1, \mathbf{r}_2, \rho_b)$ is the total macromolecule potential at position \mathbf{r}_1 . An expression for b_2 was provided by Glandt [4],

$$b_2(\mathbf{r}_1, \mathbf{r}_2, \rho_b) = \int_{\mathbf{r}'} \left\{ \exp\left[-\frac{E_m(\mathbf{r}_1, \mathbf{r}_2, \rho_b)}{kT}\right] - 1 \right\} \times \left\{ \exp\left[-\frac{U_{m-m}(\mathbf{r}_1, \mathbf{r}', \rho_b)}{kT}\right] - 1 \right\} d\mathbf{r}', \quad (3)$$

where $U_{m-m}(\mathbf{r}_1, \mathbf{r}', \rho_b)$ is the potential of mean force of two macromolecules located at positions \mathbf{r}_1 and \mathbf{r}' (both positions defined relative to the center of particle 1), respectively, and the integration is over the total system volume.

It should be noted that at sufficiently high macromolecule concentrations, Eq. (1) predicts not only a short-range depletion attraction, but also a longer-range repulsion. This repulsion arises from an ordering of the macromolecules in the gap region and is part of a more general oscillatory profile that has been predicted and measured by numerous authors [5–10]. Because only a second order virial expansion is used in the Walz and Sharma model, however, only the short-range attraction and first repulsion are predicted.

In many colloidal systems, these expressions can be simplified greatly. For example, if the macromolecule concentration is sufficiently dilute, then we can assume that both E_m and U_{m-m} are independent of the bulk number density. Second, for relatively weak or short-range potentials (such as in hard-sphere systems), we can approximate the potential of a macromolecule interacting with two particles as the sum of the individual particle–macromolecule interactions. Also, because of the spherical symmetry, the potential of a macromolecule located at position \mathbf{r}_1 relative to a particle will depend only on the distance between the particle and the macromolecule, r_1 .

Applying these approximations leads to the following expression for the interparticle depletion force

$$\mathbf{F}_1(\mathbf{r}_{12}) = - \int_{\mathbf{r}_1} \rho_b \exp\left\{-[E_{m-p1}(r_1) + E_{m-p2}(r_2)]\right\} \times [1 + b_2(\mathbf{r}_1, r_2)] \nabla_1 E_{m-p1}(\mathbf{r}_1) d\mathbf{r}_1, \quad (4)$$

where

$$b_2(\mathbf{r}_1, \mathbf{r}_2) = \int_{\mathbf{r}'} \left\{ \exp\left[-\frac{E_{m-p1}(r_1) + E_{m-p2}(r_2)}{kT}\right] - 1 \right\} \times \left\{ \exp\left[-\frac{U_{m-m}(|\mathbf{r}' - \mathbf{r}_1|)}{kT}\right] - 1 \right\} d\mathbf{r}', \quad (5)$$

where $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_1 - \mathbf{r}_{12}|$, and E_{m-p1} and E_{m-p2} denote the interaction energy between a macromolecule and particles 1 and 2, respectively.

Once the force is known, the corresponding depletion energy, $E_1(\mathbf{r}_{12})$, characterizing the interaction between two particles can be calculated as

$$E_1(\mathbf{r}_{12}) = - \int_{\infty}^{r_{12}} \mathbf{F}_1(\mathbf{r}'_{12}) \cdot d\mathbf{r}'_{12}. \quad (6)$$

Note that for spherically symmetrical systems, such as those considered below, the depletion energy, E_1 , and the magnitude of the depletion force, F_1 , will depend only on the distance between particles 1 and 2, r_{12} .

Walz and Sharma made one additional approximation to simplify the calculation of the second virial coefficient and decrease the time required for the numerical integrations. This approximation involves rewriting Eq. (5) as

$$b_2(\mathbf{r}_1, \mathbf{r}_2) = \int_{\mathbf{r}'} \left\{ \exp\left[-\frac{E_{m-p1}(r_1)}{kT}\right] - 1 \right\} \times \left\{ \exp\left[-\frac{U_{m-m}(|\mathbf{r}' - \mathbf{r}_1|)}{kT}\right] \right\} d\mathbf{r}' + \int_{\mathbf{r}'} \left\{ \exp\left[-\frac{E_{m-p2}(r_2)}{kT}\right] - 1 \right\} \times \left\{ \exp\left[-\frac{U_{m-m}(|\mathbf{r}' - \mathbf{r}_1|)}{kT}\right] \right\} d\mathbf{r}'. \quad (7)$$

Essentially, this approximation, which is demonstrated more clearly in the following section, assumes that the effects of a macromolecule interacting with two particles simultaneously can be calculated as the superposition of the effects of each particle–macromolecule interaction. In the remainder of this paper, we will analyze the validity of this approximation.

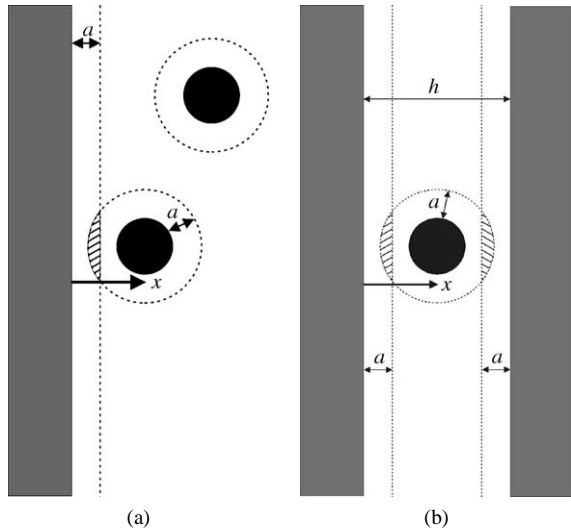


Fig. 1. These figures illustrate the physical meaning of the second virial coefficient for a macromolecule of radius a interacting with either a single wall (a) or two parallel walls (b). In (a), the value of the second virial coefficient is the volume of the hatched region. In (b), the total virial coefficient is the sum of the volume of the two hatched regions.

3. Results and discussion

3.1. The calculated second virial coefficient

The second virial coefficient has units of volume, and the physical meaning of this parameter can be easily understood by considering a system where all interactions are of the hard sphere type. Now E_m and U_{m-m} in Eq. (2) will be zero at all separations beyond hard contact and positive infinity at contact. Let us first consider the simple case of a spherical macromolecule of radius a next to a flat wall, shown in Fig. 1a. Each macromolecule excludes a spherical volume of radius $2a$ from the center of other macromolecules. The region within distance $x \leq 2a$ is excluded from the macromolecules as well. When a macromolecule approaches sufficiently close to the wall so that these excluded volumes overlap, the total excluded volume in the system is reduced by the volume of the hatched region in Fig. 1a, which is energetically favorable in a hard-sphere system. The volume of this hatched region is the second virial coefficient and this increase in the total free volume of the system results in a higher concentration of macromolecules close to the wall relative to the bulk.

Now consider the case of macromolecules in the gap region bounded by two parallel walls separated by gap width h , as shown in Fig. 1b. The issue here, which is essentially the approximation made by Walz and Sharma, is whether the virial coefficients for this system can be calculated as the simple sum of the coefficients for each wall, or specifically is $b_2(x) = b_{2,\text{wall } 1}(x) + b_{2,\text{wall } 2}(h - x)$. Geometrically, the question is whether the total change in excluded volume is equal to the sum of the changes next to each wall. For the simple case of two parallel plates, it is not difficult to see that this superposition approach is in fact al-

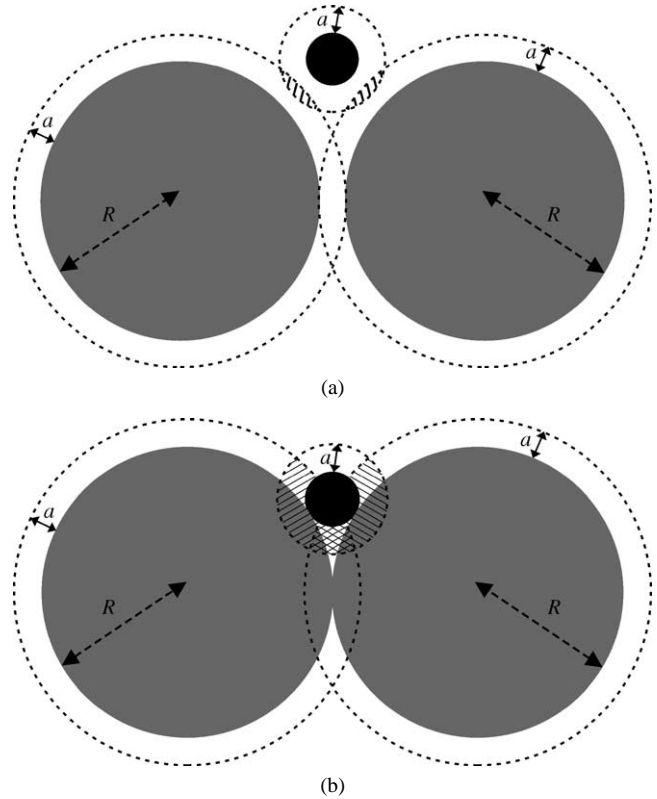


Fig. 2. These schematics illustrate the second virial coefficient for a macromolecule interacting with two spherical particles of radius R . In (a), the total coefficient is the sum of the hatched regions. In (b), however, simply summing the virial coefficient for each particle–macromolecule interaction results in overpredicting the total coefficient by the amount of the cross-hatched region.

ways valid, as the hatched regions in Fig. 2 will themselves never overlap, which is consistent with Glandt [4].

On the other hand, if the parallel walls are instead replaced by two hard spherical particles of radius R , as shown in Fig. 2a, then such a general statement cannot be made. Specifically, because the second virial coefficient at any point in the solution now depends on both the distances from the two particles and the distance from the center-to-center line between the two particles, the validity of the superposition approximation depends on position as well. For example, for macromolecules located along the center-to-center line, the additivity approach will always be true (analogous to the case of two parallel walls). The largest discrepancy, on the other hand, occurs in the arrangement shown in Fig. 2b, in which the macromolecule is touching both particles, which are themselves in contact. As can be seen, simply adding the volumes of the overlap regions of the macromolecule with each particle overpredicts the true change in excluded volume by the amount shown in the crosshatched region. Using straightforward geometry, we have calculated the volume of this crosshatched region for the particular arrangement shown in Fig. 2b and we present these results in Fig. 3. This graph plots the volume of the crosshatched region divided by the true change in the excluded volume

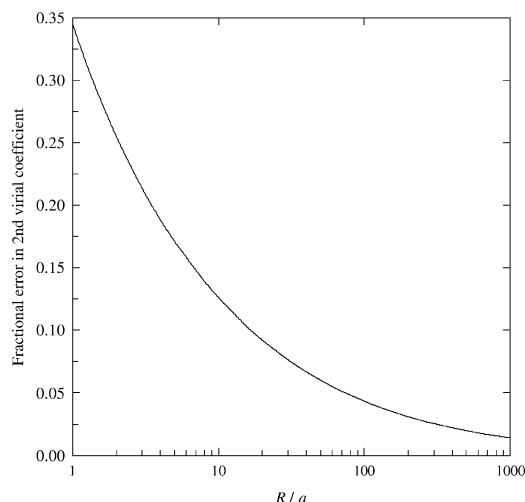


Fig. 3. This graph gives the maximum error in the second virial coefficient produced by the superposition approximation of Eq. (7). The arrangement of the particles and macromolecule is as shown in Fig. 2b, and the y-axis here is the volume of the crosshatched region in Fig. 2b divided by the true second virial coefficient. As $R/a \rightarrow \infty$, the system approaches that of two parallel plates (Fig. 1b), where the approximation is completely valid and the error is zero.

(i.e., the maximum fractional error in the second virial coefficient produced by the superposition approximation) versus the ratio of the particle to the macromolecule radii. As seen, the error is greatest when the macromolecule and particle are of equal size and drops to zero as $R/a \rightarrow \infty$. This latter result is expected, as $R = \infty$ corresponds to the case of a macromolecule between two parallel plates, where the approximation is exactly valid and the fractional error is zero.

3.2. The predicted depletion interaction

We now investigate the effect of the superposition approximation for calculating the second virial coefficient on the depletion interaction predicted with the Walz and Sharma model. First, we consider a system in which all interactions are of the hard-sphere type. Shown in Fig. 4 is the energy of interaction between two hard spherical particles of radius R in a solution of hard spherical macromolecules of radius a ($R/a = 100$ for this system) and bulk number density ρ_b as a function of the dimensionless gap width h/a , where $h = r_{12} - 2R$. Results are shown at three different macromolecule volume fractions ($\phi = 1, 3,$ and 10%) and the energies have been scaled by the factor $(3/2)\phi kT(R/a)$, which is the approximate value of the classic Asakura–Oosawa depletion interaction at contact when $R \gg a$ [11]. As seen, at all volume fractions, the energies calculated using the approximation of Eq. (7) (represented as the symbols) are essentially identical to those calculated using the complete expression of Eq. (5) (represented as lines). Thus even though the maximum error shown in Fig. 3 can be significant, integrating over all possible macromolecule positions leads to a substantially smaller error.

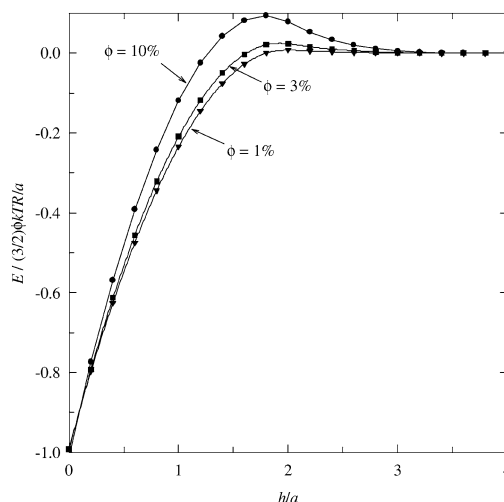


Fig. 4. This graph plots the dimensionless depletion energy between two spherical particles of radius R in a solution of spherical macromolecules of radius a and bulk volume fraction ϕ , versus the dimensionless gap width. For each plot, the solid line was calculated using the exact virial coefficient expression of Eq. (5), while the symbols were calculated using the superposition approximation of Eq. (7).

The Walz and Sharma model can also be applied to systems in which the particles and macromolecules experience longer-range (i.e., “soft”) interactions. Perhaps the most relevant for aqueous systems is the screened coulombic interaction between surfaces bearing a net electric charge. A convenient electrostatic interaction expression that can be applied to particles of essentially any size is the linear superposition expression of Bell et al. [12]. For two spherical particles of radius a_i and a_j , the interaction energy is

$$E_{\text{elec}}(r) = 4\pi\epsilon_r\epsilon_0\left(\frac{kT}{e}\right)^2 Y_i Y_j \frac{a_i a_j}{r} \times \exp[-\kappa(r - a_i - a_j)], \quad (8)$$

where r is the center-to-center distance between the spheres, ϵ_r is the relative dielectric constant of the medium, ϵ_0 is the permittivity of free space, e is the electron charge, κ^{-1} is the solution Debye length, and Y_i and Y_j are the effective surface potentials of particles i and j , respectively (the definition of the effective surface potential is given in Bell et al.). The major requirement in using this expression is that the gap width between the interacting spheres is greater than the bulk Debye length (i.e., $\kappa h > 1$, where $h = r - a_i - a_j$). The validity of this equation for calculating the depletion interaction is discussed by Piech and Walz [3].

To test the validity of the superposition approximation of Eq. (7), we considered two systems, differing in the value of κa . Each system consists of 1.5- μm radius particles and 10-nm radius macromolecules. The electric surface potential on the particles and macromolecules is -50 mV, and the macromolecule concentration is 0.35%. The bulk Debye length is 3 nm in system 1 and 15 nm in system 2, corresponding to κa values of 3.33 and 0.667. For each of these systems, we can also calculate the effective macromolecule

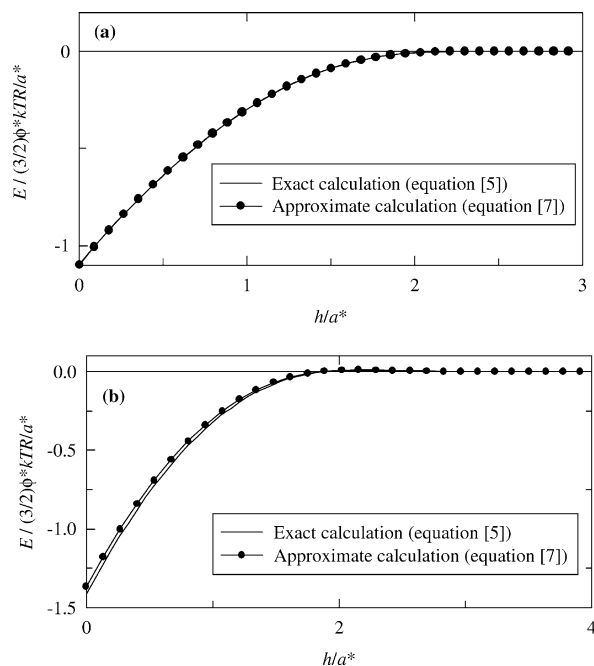


Fig. 5. These graphs show the interaction energy calculated with the Walz and Sharma model in a solution with long-range electrostatic interactions. The sizes of the particles and macromolecules are $R = 1.5 \mu\text{m}$ and $a = 10 \text{ nm}$, respectively, and both the particles and macromolecules have electric surface potentials of -50 mV . In (a) $\kappa^{-1} = 3 \text{ nm}$ and $a^* = 23.2 \text{ nm}$, while in (b), $\kappa^{-1} = 15 \text{ nm}$ and $a^* = 76 \text{ nm}$. As in Fig. 4, the solid line was calculated using Eq. (5), while the symbols were calculated with Eq. (7).

volume fraction, which utilizes an effective macromolecule size given by [13]

$$a^* = \frac{1}{2} \int_0^{\infty} \left\{ 1 - \exp\left[\frac{-E_{m-p}(r')}{kT}\right] \right\} dr', \quad (9)$$

where $E_{m-p}(r')$ is the energy of interaction between a particle and a macromolecule separated by center-to-center distance r' . Essentially, this effective size accounts for the range of the electrostatic repulsion between the individual macromolecules. Using this expression yields effective macromolecule radii of 23.2 and 76 nm for systems 1 and 2, respectively. It should be mentioned that Eq. (9) was derived assuming short-range interactions and is thus only approximate for the system with 15 nm Debye length. Piech and Walz [14] showed that the effective thickness of the charged double layer could also be calculated as the particle–macromolecule gap width where the electrostatic repulsive energy between the particle and macromolecule equals $0.5kT$. Using this approach yields effective macromolecule sizes of 23.8 and 77.8 nm for the 3- and 15-nm Debye length systems, respectively, which are very close to the values obtained by Eq. (9).

The calculated interparticle depletion energies for these two systems are shown in Fig. 5. The gap width between the particles, h , is scaled by the effective macromolecule radius, a^* , and the interaction energy is scaled by the ef-

fective Asakura–Oosawa contact energy, $(3/2)\phi^*kTR/a$. (Note that this effective size is used only in scaling the separation distance and resulting energy; the calculation of the interaction energy was made using the actual electrostatic interaction expression given in Eq. (8).) As seen, in both systems, the energies calculated using the approximate second virial coefficient expression of Eq. (7) (symbols) are in very good agreement with those calculated using the exact approach of Eq. (5) (lines). Specifically, at the smallest separations, the error between the two methods is less than 2%. These results show clearly that the superposition approximation can be employed in systems with long-range interactions as well.

4. Conclusions

We have examined the validity of an approximate method for calculating the second virial coefficient for a macromolecular solution bounded by two interfaces. Specifically, the effect of the approximation on the depletion interaction between two spherical particles was examined in systems with both hard-sphere and long-range interactions. In all systems studied, the results calculated with the approximate model were found to be in good agreement with those obtained using an exact expression for the second virial coefficient. The advantage of this approximate approach is a significant savings in the computation time required to calculate the interparticle depletion interaction.

These results also showed that the expression for predicting the depletion interaction in purely hard-sphere systems can also be used in dilute ionic systems, provided the appropriate effective macromolecule size is used. This can be seen by the similarities between the curve at 1% volume in Fig. 4 (purely hard-sphere system) and the curve in Fig. 5a (charged system). Specifically, the scaled attractive energy is approximately -1 at contact and the interaction extends to a scaled separation distance of approximately 2. The discrepancies from these values seen in the curves result primarily from the effects of second order concentration effects, which are not included in the scaling factors. In addition, this scaling demonstrates that for the attractive depletion interaction, the correct macromolecule size is determined by the range of the interaction between the particles and nonadsorbing macromolecules (as given in Eq. (9)), as opposed to the interaction between the macromolecules themselves.

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