

Virial Coefficients for Hard Spheres Immersed in Hard Rod Solutions

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Abstract

Many systems such as protein-virus systems can be modeled simply as a mixture of hard spheres in a hard rod solution. There is an effective two-body attractive force between spheres due to the overlap of exclusion volumes from a rod by two spheres close to each other. We calculate the overlap volume of these exclusion volumes, two parallel spherocylinders, in a one-dimensional integral representation, where the integration is over the direction of the axes of the spherocylinders. The effective attractive potential is then calculated from an angular average of these overlap volumes. The calculation can be performed both for infinitely thin rods and for rods of finite thickness when those rods are modeled as spherocylinders. From a third integration over distance, we calculate the second virial coefficient of this system for a variety of length-to-radius ratios, rod-to-sphere radius ratios, and rod densities. Some observations are presented also on three-body effects and the presence of a repulsive, non-additive three-body potential.

1. Introduction

The system of hard spheres of radius R immersed in a solution of hard rods of length L has been of interest as a model of protein-virus and other systems [1]. There is an effective attractive potential energy between two hard spheres from the depletion volume due to the rods. The volume excluded to the center of mass of a rod by a sphere is a spherocylinder, composed by a cylinder of length L and radius R with hemispherical caps of radius R at each end. In a sufficiently dilute system, these spherocylindrical exclusion volumes are nonoverlapping and independent. However, for two hard spheres sufficiently close to each other (the distance between their centers must be greater than $2R$), the exclusion volumes for a rod of a given orientation can overlap each other. The net volume excluded from the rod by the two spheres is less than twice the individual exclusion volume for a dilute system, and this results in an effective attractive interaction. The interaction has been calculated in the limits $L/R \gg 1$ [2] and $L/R \ll 1$ [3].

To our knowledge, there is no known analytic expression for the overlap volume of two parallel spherocylinders. In this paper, we derive a one-dimensional integral representation of this overlap volume for a given geometry. In coordinates where z is parallel to the spherocylinder axes, slices of the overlap volume in planes of constant z are various cases of circle-circle overlap. The areas of these are calculable analytically, and in general only numerical integration over z is needed to find the volume of overlap for a fixed orientation of the rod.

It is assumed that the orientation distribution of the rods is isotropic, though other distributions could be considered. Calculation of the effective potential between two spheres then requires a second numerical integration over angle. We proceed to calculate the second virial coefficient of a moderately dense system of spheres in a solution of rods, which requires a third numerical integration over angle. Yaman et al. [1] derived by a different method a two-dimensional representation of the two-body potential, but their method is not applicable to rods of finite thickness.

We are also interested in the third virial coefficient, the calculation of which involves considering the overlap volume of three spherocylinders. This leads to a net repulsive potential, and results will be presented elsewhere. In this paper we only consider two-body interactions and the second virial coefficient.

2. Interaction Potential

The free energy F of a system of hard spheres immersed in a fluid of rods is

$$F = -k_B T \ln \Omega \quad (1)$$

where k_B is Boltzmann's constant, T is absolute temperature, and Ω is the number of configurations available to the rods in the system. If we make the approximation that the rods only interact with the spheres and not with each other, then the number of configurations is given by

$$\Omega = (V - V_{ex})^{N_B} = V^{N_B} (1 - c_B V_{ex}/N_B)^{N_B} \quad (2)$$

where V is the total volume of the system, V_{ex} is the average volume excluded from the rods by the spheres, N_B is the total number of rods in the system, and $c_B = N_B/V$ is the concentration of rods. In the thermodynamic limit (i.e., N_B and $V \rightarrow \infty$ while c_B is constant)

$$\Omega = V^{N_B} \exp(-c_B V_{ex}) \quad (3)$$

In the case of two spheres, an effective interaction arises between the spheres, because the volume excluded from the rods by the spheres is greater when the spheres are infinitely separated than when they are close to each other (i.e., $2V_{ex}^{(1)} \geq V_{ex}(r)$, where $V_{ex}^{(1)}$ is the volume excluded by the rod by a single, isolated sphere, and $V_{ex}(r)$ is the volume excluded by two spheres separated by a distance r , due to the overlap of the excluded volumes when the spheres are close. As a result, when the spheres are close to each other the free energy of the system is lower. The effective interaction $u^{(2)}(r)$ of two spheres separated by a distance r is given by

$$\begin{aligned} u^{(2)}(r) &= F(r) - F(\infty) \\ &= k_B T c_B [V_{ex}(r) - 2V_{ex}^{(1)}] \\ &= -k_B T c_B \langle V_{ol}(r) \rangle \end{aligned} \quad (4)$$

where $\langle V_{ol}(r) \rangle$ is the average volume of overlap between the volumes excluded by two spheres. Because $V_{ex}(\infty) > V_{ex}(r)$, it follows that $\langle V_{ol}(r) \rangle \geq 0$, and the interaction is attractive.

In the following section we explain how, for a given rod orientation, V_{ol} can be expressed in a one-dimension numerical integral representation.

3. Geometry of Spherocylinder Overlap

The overlap volume V_{ol} excluded from a particular rod in Eq. (4) is the overlap volume of two parallel spherocylinders oriented in the direction of the rod, each of length L and radius R . Each spherocylinder is a cylinder with hemispherical caps of radius R at

each end. Our coordinate system is Cartesian with z along the cylinder axes and $x=0$ in the plane of the two axes.

A slice of the overlap volume in a plane of constant z is the area of circle-circle overlap. This overlap can be calculated analytically in all cases. Finding the overlap volume requires an integral over z , which can in some cases be calculated analytically but in general must be calculated numerically.

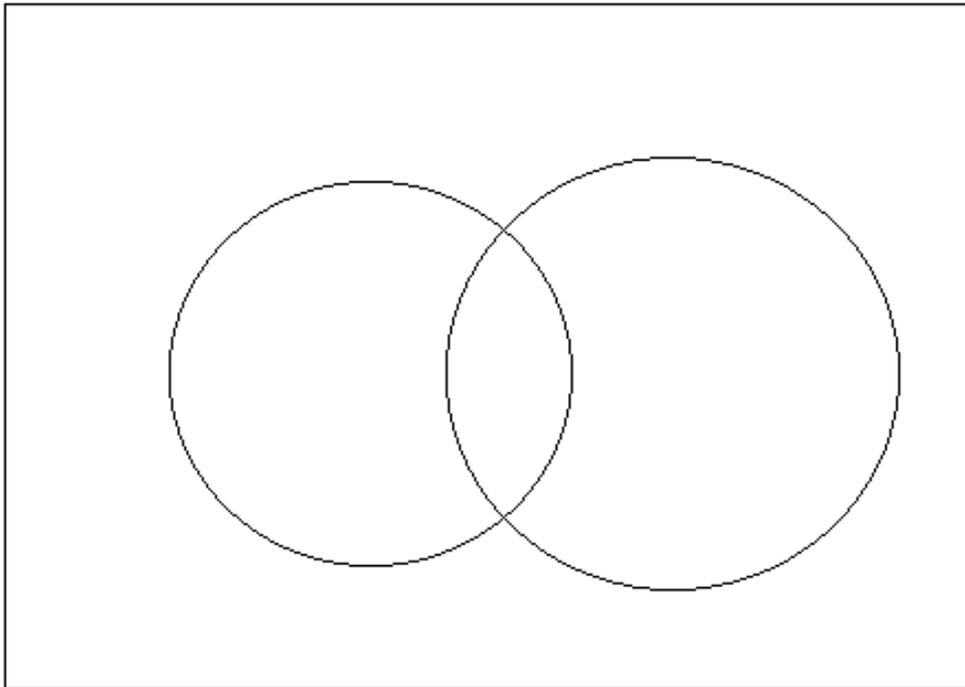


Figure 1. Segment-segment overlap.

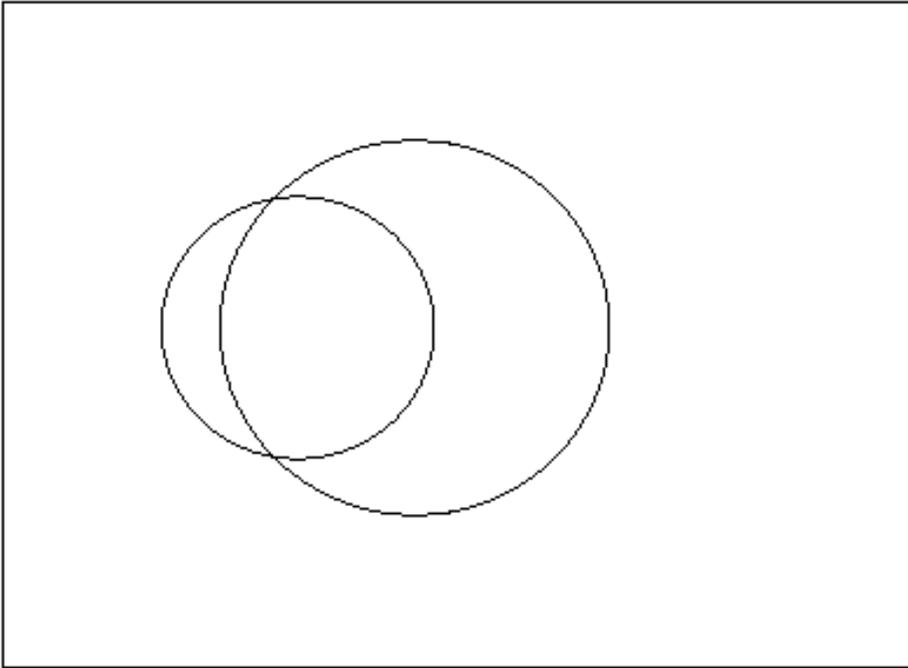


Figure 2. Segment – majority small circle overlap.

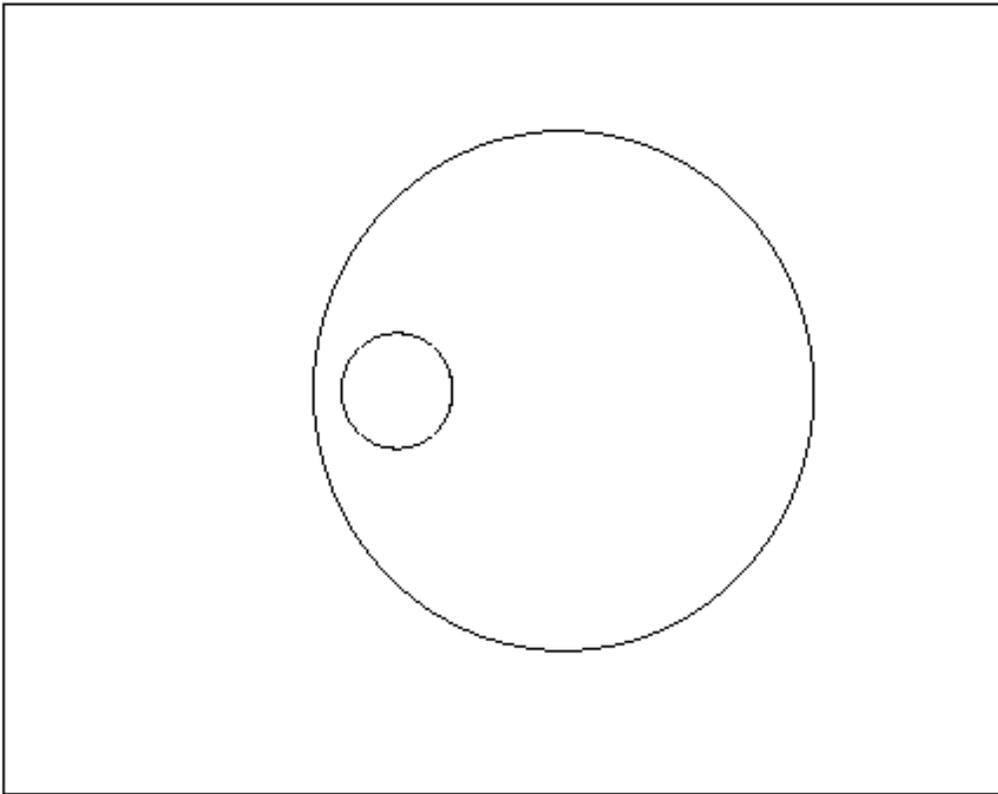


Figure 3. Full small circle overlap.

Figures 1-3 show the three possible cases of circle-circle overlap: segment-segment, segment-majority small circle, and full small circle. A segment is the region between a chord and an arc (less than π radians). If the radius of the arc is R and half of the chord length is h , the area of the segment is:

$$A = R^2 \cos^{-1}(h/R) - h(R^2 - h^2)^{1/2} \quad (5)$$

Segment-majority small circle overlap is shown in Fig. 2, where the arc length of the circle of smaller radius in the overlap region is greater than π . In this case, the area contributed by the smaller circle is that of the full circle minus a segment. Finally, the large circle can completely enclose the small circle as in Fig. 3.

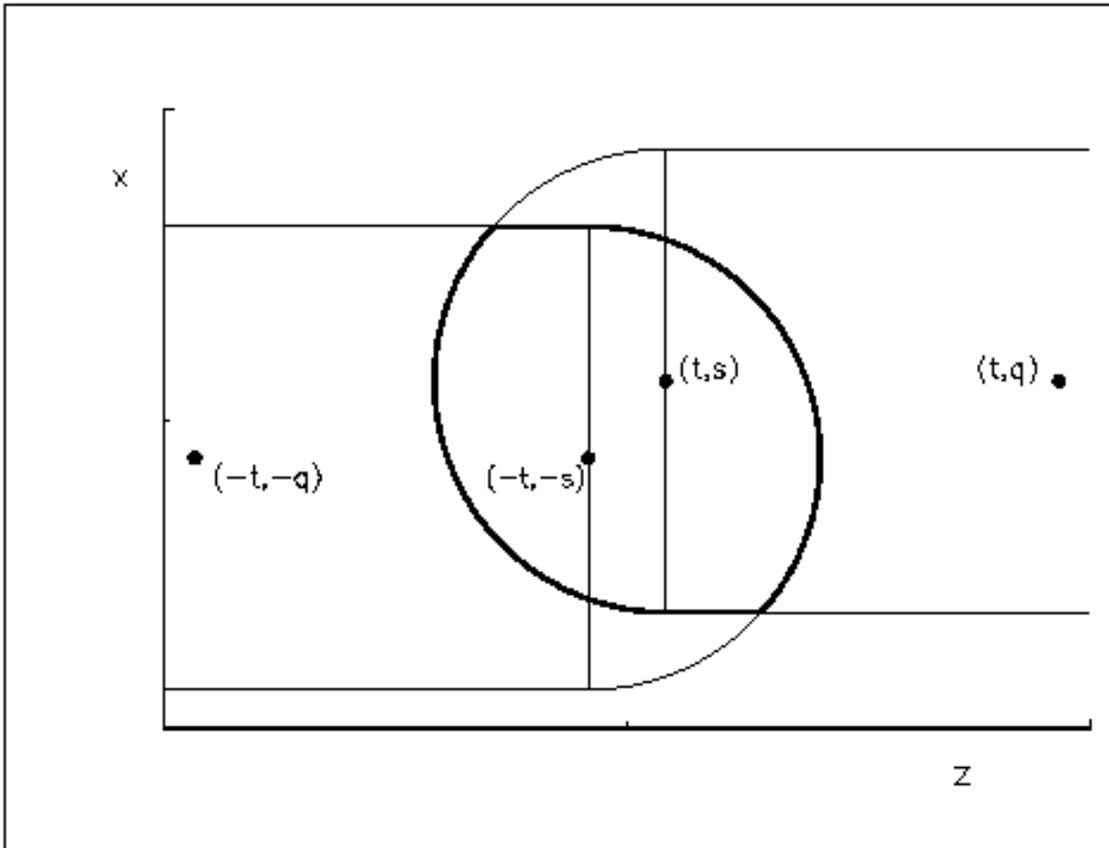


Figure 4. Spherocylinder-spherocylinder overlap. The overlap region is outlined in bold.

Our geometry is shown in Fig. 4. We place the center of spherocylinder 1 at $(-t,0,-q)$ and the center of spherocylinder 2 at $(t,0,q)$, where overlap occurs only if $0 < t < R$. The centers of the circles joining the cylinders and caps are at $(-t,0,-s)$ and $(t,0,s)$, where

$$2s = 2q - L \quad (6)$$

If s is negative we have cylinder-cylinder and cylinder-cap overlap, while if s is positive and $s^2 + t^2 < R^2$ we have cylinder-cap and cap-cap overlap, or just cap-cap overlap.

The overlap volume is symmetric about the origin, so we need only consider the half in the region $z > 0$. In a plane of constant z , we have overlap of circles from the two spherocylinders of radii r_1 and r_2 respectively, where for $z > 0$, $r_1 < r_2$.

In the case $s < 0$, if $z < |s|$, then $r_1(z) = r_2(z) = R$. The cylinder-cylinder overlap volume is simply $4A|s|$, where A is the segment area given by Eq. (A1) with $h = (R^2 - t^2)^{1/2}$.

For $z > |s|$,

$$r_1(z) = [R^2 - (z - |s|)^2]^{1/2} \quad (7)$$

and

$$r_2(z) = R. \quad (8)$$

If $t < R/2$, in an x-y plane of constant z , the overlap volume consists of two segments of unequal radii but with the same chord length $2h$. In this plane, r_1 , r_2 , and $2t = T$ form a triangle, and h is the altitude of this triangle perpendicular to the side of length t . We calculate this altitude from the formula for the area of a triangle in terms of its sides, where $S = r_1 + r_2 + T$.

$$Th / 2 = [S(S - 2r_1)(S - 2r_2)(S - 2T)]^{1/2} / 2 \quad (9)$$

In this case,

$$h = [T^2(R^2 - z^2/2) - (z^4 + T^4)]^{1/2} / T \quad (10)$$

For $s < 0$, the cylinder-cylinder overlap volume is found analytically as

$$V_{ol} = 2|s|[R^2 \cos^{-1}(t/R) - t[R^2 - t^2]^{1/2}] \quad (11)$$

The cylinder-cap part of the overlap must be found by numerical integration over z of the cross-sectional area, from a lower limit of $z = s$. For $R/2 < t < R$, this integral is broken into two parts, the part of segment-segment overlap and that of segment-majority small circle overlap. The transition occurs where r_1 , r_2 and T form a right triangle, which occurs at $z = 2s$. The maximum z is $z_{max} = s + 2(tR - t^2)^{1/2}$.

For the case $t < R/2$, as z increases from 0 the cross-sections are successively segment-segment, segment - majority small circle, and full small circle, which occurs from $z = z_{max}$ to $z = R + s$. This last volume may be expressed analytically. A spherical cap from $z = z_0$ to $z = R$ of a sphere of radius R centered at the origin has a volume

$$V = \pi(2R^3/3 - R^2z_0 + z_0^3/3) \quad (12)$$

For positive s , there is either cap-cylinder and cap-cap overlap, or pure cap-cap overlap, in which case the overlap volume is analytically calculable from Eq. (12). For cross-sections of circle-circle overlap with cap-cap overlap, Eq. (7) still applies for r_1 , but in this case, instead of Eq. (8), we have

$$r_2(z) = [R^2 - (z + s)^2]^{1/2} \quad (13)$$

and Eq. (9), but not Eq. (10), applies for the geometry of overlap.

In all cases, $r_1 = r_2$ at $z = 0$, so as z increases the circle-circle overlap evolves from segment-segment, to segment-majority small circle, to (if $t > R/2$) full small circle. There are several different cases, depending on where the two transition values of z are located relative to the cap-cylinder plane, but all involve one-dimensional integrals over z . Even when there is cap-cylinder overlap, in some cases the overlap is only between the spherical extensions of the hemispherical caps, so Eq. (12) is applicable.

4. Angle and interparticle distance integrations

We consider the effective depletion force between two hard spheres of radius R and a polar coordinate system where the z axis is aligned along the vector \mathbf{r} between their centers. The overlap volume depends on r (magnitude) and θ but is independent of φ , the azimuthal angle. The transformation to t and q is

$$t = (r \sin \theta) / 2 \quad (14)$$

$$q = (r \cos \theta) / 2 \quad (15)$$

with s given by Eq. (6). For a given r and θ , V can be calculated by numerical integration over z as described above. The angle-averaged overlap volume is

$$\langle V(r) \rangle = \int_0^{\theta_{\max}} V(r, \theta) \sin \theta d\theta \quad (16)$$

where

$$\begin{aligned} \theta_{\max} &= \sin^{-1}(2R/r) \quad \text{if} \quad 2R < r < (L^2 + 4R^2)^{1/2} \\ \theta_{\max} &= \cos^{-1}[(L^2/2 + r^2/2 - 2R^2)/rL] \quad \text{if} \quad (L^2 + 4R^2)^{1/2} < r < L + 2R \end{aligned} \quad (17)$$

Since the spheres are hard, no overlap is possible for $r < 2R$, and no overlap of the spherocylinders is possible for $r > L + 2R$.

In general, for multidimensional integration it is more efficient to use Monte Carlo integration in more than 4 dimensions, but to use numerical quadrature in fewer than 4 dimensions if the integration limits are known and the integrands are reasonably smooth. As described above, in the z -integration to calculate V_{oi} , we split the integration region into intervals so that the integrands are analytic within each interval.

We use Clenshaw-Curtis quadrature [7], which has been used extensively in calculation of collision integrals within the kinetic theory of gases [8,9], and which has the advantage that a reliable error estimate is calculated along with the integral value. For z -integration, we set the error estimate as a part in 10^4 , which typically requires a quadrature of 8, 16, or 32 intervals. As a check, we have independently calculated overlap volumes for selected specific cases by Monte Carlo integration for which the code is considerably simplified, with agreement consistent with Monte Carlo error estimates. For integration over θ and subsequent integration over r , since the integrands are not strictly multiply differentiable, we use 64-point quadrature. From our experience, integration error should be within a factor of 3 of the Clenshaw-Curtis error prediction.

When $2R < r < 2R + L$, the effective attractive potential between spheres is proportional to the angular average of the overlap volume. The second virial coefficient of such a system with c_B rods per unit volume is given by

$$B = 2\pi \left\{ \int_0^{2R} r^2 dr + \int_{2R}^{2R+L} r^2 dr [1 - \exp(c_B \langle V(r) \rangle)] \right\} \quad (18)$$

Although the thermophysical properties of a particular hard-body system are independent of temperature, here c_B plays a role similar to the usual role of $\beta = 1/k_B T$ in thermodynamics.

This integral can be evaluated rapidly by multiple Clenshaw-Curtis quadrature. Results for a variety of L and c_B for $D = 0$ are given in Table 1. From the Clenshaw-Curtis error estimate, with allowances made for higher derivative discontinuities in the integrand, our results are estimated to be accurate to at least within a part in 10^5 .

5. Calculation for Thick Rods

The discussion to this point has been for infinitely thin rods. We now consider rods of some small radius D , where $D \ll R$. We choose to model these rods as spherocylinders of length L , so the volume excluded to a rod by a sphere is again a spherocylinder, of length L and radius $R + D$. We retain the approximation that rod-rod interactions may be neglected.

We assume both the spheres and the rods are dilute, and therefore the volume fraction of each is much less than one. This implies that

$$c_B \pi D^2 L \ll 1 \quad (19)$$

We will impose the restriction that the rod volume fraction is less than 0.2, and also that $D/R < 0.2$.

The calculation is basically the same as before, except that while the exclusion volumes can overlap if $r > 2R$, those spherocylinders have radius $R + D$, and the upper limit of integration of Eq. 16 is now $2R + 2D + L$, and Eq. 15 becomes

$$\begin{aligned} \theta_{\max} &= \pi/2 & \text{if } 2R < r < 2(R + D) \\ \theta_{\max} &= \sin^{-1}[2(R + D)/r] & \text{if } 2(R + D) < r < [L^2 + 4(R + D)^2]^{1/2} \\ \theta_{\max} &= \cos^{-1}\{[L^2/2 + r^2/2 - 2(R + D)^2]/2rL\} & \text{if } [L^2 + 4(R + D)^2]^{1/2} < r < L + 2(R + D) \end{aligned} \quad (20)$$

Table 1 also lists calculated values of the second virial coefficient for finite D .

6. Conclusions

We have derived a two-dimensional integral representation of the depletion force in a system of hard spheres and hard rods, both infinitely thin and of finite thickness. From this, we have calculated by numerical quadrature the second virial coefficient of that system for a variety of parameter values. In future work, we will present a similar

calculation of the third virial coefficient, including a nonadditive, repulsive contribution. While theoretical results have suggested the occurrence of flocculation in this system, experimental results have not shown flocculation [10,11]. We are in agreement with Yaman et al. [1] that direct calculations of the potential for all L/R can lead to different conclusions than approximations to the potential. Furthermore, the nonadditive, repulsive three-body term in the potential should also serve to inhibit flocculation.

References

1. K. Yaman, C. Jeppesen, and C. M. Marques, *Europhys. Lett.* **42**, 221 (1998).
2. L. Auvray, *J. Physique* **42**, 79 (1981).
3. Y. Mao, M. E. Cates, and H. N. W. Lekkerkerker, *Phys. Rev. Lett.* **75**, 4548 (1995).
4. K. Yaman, M. Jeng, C. Jeppesen, P. Pincus, and C. M. Marques, *Physica A* **247**, 159 (1997).
5. K. Yaman, P. Pincus, and C. M. Marques, *Phys. Rev. Lett.* **78**, 4514 (1997)
6. P. Bolhuis and D. J. Frenkel, *J. Chem Phys.* **101**, 9869 (1994).
7. C. W. Clenshaw and A. R. Curtis, *Numer. Matl.* **2**, 197 (1960).
8. H. O'Hara and F. J. Smith, *J. Comput. Phys.* **5**, 328 (1970).
9. J. C. Rainwater, P. M. Holland, and L. Biolsi, *J. Chem. Phys.* **77**, 434 (1982).
10. M. A. Tracy, J. L. Garcia, and R. Pecora, *Macromolecules* **26**, 1862 (1993).
11. T. Biben, P. Blandon, and D. Frenkel, *J. Phys. Condens. Matter* **8**, 10799 (1996).

Table 1: Second Virial Coefficient

L/R	c_B	B/R^3			
		D = 0.00	D = 0.05	D = 0.10	D = 0.15
1.0	0.10	16.519	16.469	16.414	16.353
1.0	0.20	16.279	16.176	16.062	15.938
1.0	0.50	15.533	15.261	14.951	14.609
1.0	1.00	14.206	13.603	12.892	12.080
2.0	0.10	15.389	15.345	15.294	15.238
2.0	0.20	13.973	13.876	13.762	13.636
2.0	0.50	9.394	9.074	8.686	8.246
2.0	1.00	0.491	-0.493	-1.733	-3.203
5.0	0.10	5.790	6.313	6.747	7.112
5.0	0.20	-6.005	-5.002	-4.190	-3.526
5.0	0.50	-47.559	-45.595	-44.299	-43.534
5.0	1.00	-148.059	-148.917	-153.167	-160.665
10.0	0.10	-31.331	-28.016	-25.181	-22.732
10.0	0.20	-84.963	-78.475	-73.028	-68.413
10.0	0.50	-297.444	-285.683	-278.515	-275.261
10.0	1.00	-1106.890	-1199.623	-1374.450	-1650.265