An effective-colloid pair potential for Lennard-Jones colloid–polymer mixtures

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We propose an effective one-component model that accurately reproduces the colloid–colloid radial distribution function $g_{cc}(r)$ of a colloid–polymer mixture. The particles of this effective model interact through an effective potential $u_{\text{eff}}(r)$, obtained by inversion of the Ornstein–Zernike equation and a closure suited for fluids with repulsive cores. The consistency of this approach was tested by simulation of the effective one-component fluid and comparison to the original radial distribution function. The effective potential can be separated into a repulsive part (corresponding to the “bare” pair potential between colloids), and a depletion potential, $v(r)$. The strength and range of $v(r)$ are well represented by simple functions of the total volume fraction. © 2003 American Institute of Physics. [DOI: 10.1063/1.1533787]

I. INTRODUCTION

Two colloidal particles interacting through a purely repulsive potential may experience an attractive force when suspended in a macromolecular fluid due to depletion forces.¹ These depletion forces are important because they introduce a mechanism for inducing phase separation and flocculation in systems without “bare” attractive forces.² Among these systems, colloid–polymer mixtures (CPM) have been studied by a diversity of theoretical,^{3,4} experimental,^{5–7} and simulation^{8,9} methods.

The depletion forces are well known from the theory of liquids since the work of Asakura and Oosawa, arising from volume exclusion effects.¹ From this perspective, the depletion forces between colloids are entropically driven interactions that can be obtained by integrating out the degrees of freedom of the macromolecular component. By employing hard-sphere models for colloid–polymer mixtures, Evans *et al.* have used a density functional theory approach to map highly asymmetric mixtures to an effective one-component potential for the colloids.⁶ Their approach is exact when the size ratio $q = R_g/R_c < 0.1547$, where R_g is the radius of gyration of the polymer and R_c is the radius of the colloids.

Another approach is that of Louis and co-workers,^{9–12} based on the inversion of radial distributions functions (RDF) $g(r)$ for the centers-of-mass of colloids and polymer chains. Through inversion of the Ornstein–Zernike (OZ) equation with a hypernetted chain (HNC) closure, they arrived at effective potentials for the polymer–polymer and polymer–colloid interactions in a binary CPM, and obtained the phase diagram for these coarse-grained models by Gibbs–Ensemble Monte Carlo simulations.¹³

In this work we take an additional step in the coarse graining hierarchy and show that an effective, one-component potential for colloids suspended in a CPM can be defined. Instead of the HNC closure, we use a different one that is better suited to potentials with strong repulsive cores.

The effective one-component system radial distribution, obtained by Monte Carlo simulation, is compared to that of the colloids in the original CPM. Finally, the effective potential is analyzed into its repulsive and attractive parts, and the dependence of the strength and range of the effective depletion potential with composition are analyzed.

II. SIMULATION OF THE COLLOID–POLYMER MIXTURE

The system under study is a mixture of spherical colloids and polymer chains, each chain consisting of L spherical monomers. The basic interactions are the three pair potentials between the colloids and monomer units [$u_{cc}(r)$, $u_{cm}(r)$, $u_{mm}(r)$] and the bonding potential for neighboring monomers in a chain, $u_b(r)$.

All these interactions are purely repulsive. The nonbonding interactions are of the Lennard-Jones (LJ) type, truncated and shifted at the minimum,

$$u_{ab}(r; \sigma_{ab}, \epsilon_{ab}) = 4\epsilon_{ab} \left(\left(\frac{\sigma_{ab}}{r} \right)^{12} - \left(\frac{\sigma_{ab}}{r} \right)^6 \right) + \epsilon_{ab};$$

$$r < 2^{1/6} \sigma_{ab},$$

$$u_{ab}(r; \sigma_{ab}; \epsilon_{ab}) = 0; \quad r \geq 2^{1/6} \sigma_{ab}. \quad (1)$$

Parameters σ and ϵ represent a characteristic range σ_{ab} and strength ϵ_{ab} . The bonding energy of interaction between monomers is a repulsive function of harmonic form,

$$u_b(r; \sigma_{mm}, k_h) = k_h(r - 2^{1/6} \sigma_{mm})^2/2. \quad (2)$$

In this work we have set the chain length to $L=100$, and the elastic constant to $k_h = 10^4$. The values for the diameters σ_{ab} and energies ϵ_{ab} are shown in Table I. All energies ϵ_{ab} are equal, and the colloid size is one order of magnitude larger than the size of a monomer.

We simulated the system at a temperature that makes the Barker–Henderson mean collision diameters:¹⁴

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TABLE I. Parameters of the nonbonding potentials.

a	b	σ_{ab}/σ_{mm}	$\epsilon_{ab}/\epsilon_{mm}$
monomer	monomer	1	1
monomer	colloid	6	1
colloid	colloid	11	1

$$d_{ab}^{\text{BH}}(\beta) = - \int_0^\infty (e^{-\beta u_{ab}(r)} - 1) dr, \quad (3)$$

equal to σ_{ab} for the three nonbonded potentials. This special temperature is given by $k_B T^{\text{BH}}/\epsilon_{ab} = 15.079$. This facilitates comparison of our results to available findings for hard-spheres.

We performed off-lattice canonical Monte Carlo simulations with a fixed number of colloids (N_c) and polymer chains (N_p) in a periodic, cubic box of constant volume V , at constant temperature, T . A typical simulation contains a hundred colloids and several hundred polymer chains. Trial configurations were generated through a combination of reptation and configuration bias moves for the chains, and random displacements of colloids and monomers.

The polymer concentration can be characterized as dilute when the polymer density is smaller than

$$\rho_p^* = (4\pi R_g^3/3)^{-1}. \quad (4)$$

The quantity ρ_p^* is called the overlap density and represents an approximate upper limit for the dilute regime. Since R_g depends on $\rho_p = N_p/V$, it is often convenient to define the overlap density using $R_g = R_{g0}$, the radius of gyration of an isolated chain. Thus, the ratio ρ_p/ρ_p^* corresponds to the packing fraction η_p for spheres of radius R_{g0} at density ρ_p ,

$$\eta_p = (4\pi R_{g0}^3/3)\rho_p. \quad (5)$$

The packing fraction becomes greater than unity as the system enters the semidilute regime. In order to determine R_{g0} , a simulation of an isolated chain was performed, with the result $R_{g0} = 7.558\sigma_{mm}$. For the colloids, we express concentration in terms of the colloid volume fraction

TABLE II. Simulation results, with the estimated uncertainty in the last decimal place given in parentheses.

State	η_p	η_c	R_g/σ_{mm}	$10^{-5}U/\epsilon_{mm}$	$\beta\mu^{\text{inc}}$
I	9.8×10^{-6}	0.0000	7.5578(2)	0.00783(1)	0.28744(9)
A0	0.0097	0.03358	7.5990(7)	0.314(2)	0.29183(5)
A1	0.0871	0.06715	7.5470(2)	0.393(9)	0.29589(7)
A2	0.1830	0.06715	7.5077(7)	0.825(2)	0.29983(7)
A3	0.3659	0.06715	7.4779(2)	1.65(5)	0.30836(1)
A4	0.7318	0.06715	7.3279(1)	3.3(1)	0.32930(3)
B1	0.2832	0.14552	7.3979(6)	0.59(1)	0.31459(3)
B2	0.5664	0.14552	7.2928(2)	1.189(3)	0.33324(7)
B3	1.1328	0.14552	7.0895(3)	2.38(5)	0.37894(2)
B4	1.2461	0.14552	7.0033(7)	2.63(8)	0.38677(6)
C1	0.2058	0.17244	7.3972(3)	0.365(4)	0.31380(4)
C2	0.4072	0.17244	7.3155(2)	0.72(1)	0.32700(5)
C3	0.8144	0.17244	7.1343(2)	1.45(5)	0.35687(2)

FIG. 1. The radial distribution function between polymer centers of mass, $g_{pp}(r)$, at the states of Table II. (a) A1 (solid), A2 (dotted-dashed), A3 (dotted), and A4 (dots); (b) B1 (solid), B2 (dotted-dashed), B3 (dotted), and B4 (dots); (c) C1 (solid), C2 (dotted), and C3 (dots).

$$\eta_c = \frac{\pi\sigma_{cc}^3}{6}\rho_c. \quad (6)$$

The simulations were performed at the values of η_p and η_c listed in Table II. This same table shows results for R_g , the total potential energy (U), and the incremental chemical potential ($\beta\mu^{\text{inc}}$) of the polymer. The potential energy and the radius of gyration were computed by ensemble averaging; their statistical errors were estimated using block averages by the Flyvbjerg-Petersen method.¹⁵ The excess chemical potential was calculated by the method of incremental Rosenbluth appending of Escobedo and de Pablo,¹⁶ using up to four appended monomers.

For all simulations, we computed the three radial distribution functions between centers-of-mass of colloids and polymer chains, $g_{cc}(r)$, $g_{cp}(r)$, and $g_{pp}(r)$. Some of these functions are shown in Figs. 1–3.

FIG. 2. The polymer–colloid radial distribution function, $g_{cp}(r)$, at the states of Table II. Symbols as in Fig. 1.

III. EFFECTIVE COLLOID POTENTIAL BY INVERSION OF $g_{cc}(r)$

An effective one-component fluid can be introduced whose particles interact via an effective potential $u_{\text{eff}}(r)$. This potential is defined by the requirement that the relation $g(r) = g_{cc}(r)$ be satisfied at the same values of η_c and β as those of the colloid–polymer mixture.

For a one-component fluid, the Ornstein–Zernike equation,¹⁴

$$h(r) = c(r) + \rho \int h(r') c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (7)$$

relates the total correlation function $h(r) = g(r) - 1$ to the direct correlation function $c(r)$. The connection between the correlation functions and the pair potential $u(r)$ is made by the “closure” relation,

$$g(r) = \exp(-\beta u(r) + h(r) - c(r) + B(r)). \quad (8)$$

The exact form of the closure is given by the form of the bridge function $B(r)$; this is usually done as a functional

FIG. 3. The colloid–colloid radial distribution function $g_{cc}(r)$ at the states of Table II. Symbols as in Fig. 1.

$$B(r) = \mathcal{B}(s(r)) \quad (9)$$

of the series function

$$s(r) = h(r) - c(r). \quad (10)$$

As an instance, the HNC closure corresponds to

$$\mathcal{B}(s) = 0. \quad (11)$$

The effective potential can be obtained from Eq. (8) by setting $u(r) = u_{\text{eff}}(r)$,

$$\beta u_{\text{eff}}(r) = -\ln g(r) + h(r) - c(r) + \mathcal{B}(h(r) - c(r)). \quad (12)$$

It is important to note that $\beta u_{\text{eff}}(r)$ differs from the potential of mean force $\beta w(r) = -\ln g(r)$ due to the presence of the term $s(r) + \mathcal{B}(s)$ in Eq. (12).

As mentioned earlier, the HNC closure has been used by Bolhuis and co-workers along with the OZ equation to define effective potentials between the center-of-mass of two polymers, or a polymer and a colloid.^{9–13} However, the HNC closure is not particularly accurate for strongly repulsive in-

interactions such as hard-sphere or Lennard-Jones potentials between two colloids.¹⁷ A good alternative in this latter case is the Duh–Henderson (DH) closure,

$$\begin{aligned} \mathcal{B}(s) &= -\frac{(9+7s)}{(3+s)(3+5s)}s^2/2; \quad s > 0, \\ \mathcal{B}(s) &= -s^2/2; \quad s \leq 0, \end{aligned} \quad (13)$$

which was developed for LJ fluids by inverting $\mathcal{B}(s)$ data from simulation and has been shown to give excellent results.¹⁸

There are other commonly used closures that could have been used in the inversion procedure: in particular, the mean spherical approximation (MSA),^{19,20} Martynov–Sarkisov (MS),^{21,22} and modified-Verlet (MV)²³ closures have been extended from their original hard-sphere version of Lennard-Jones fluid variants. However, $s(r)$ is small outside of the repulsive core. The Taylor expansion of $\mathcal{B}(s)$ for the MSA, MS, MV, and DH closure agree to leading order,

$$\mathcal{B}(s) = -0.5s^2 + O(s^3). \quad (14)$$

This means that the inversion procedure employed here could not be sensitive to the replacement of the DH closure by the MSA, MS, or MV closures, except deep inside the core.

Using the DH closure, we inverted the simulated RDF between colloids $g_{cc}(r)$ in the colloid–polymer mixture in order to obtain the corresponding effective potentials. In the limit $\eta_p \rightarrow 0$ we expect $u_{\text{eff}}(r) = u_{cc}(r)$, and therefore introduce an effective depletion potential defined by

$$v(r) = u_{\text{eff}}(r) - u_{cc}(r). \quad (15)$$

Figure 4 depicts $\beta v(r)$ for several simulated states. One can see that $v(r)$ is attractive, and approaches zero within a few R_{g0} beyond $r = \sigma_{cc}$. As the polymer concentration is increased, the range of $v(r)$ diminishes and its strength grows. However, close to the overlap density, $v(r)$ appears to develop a small positive maximum.

In order to test the consistency of the effective colloid potentials, we performed new canonical Monte Carlo simulations at the values of η_c shown in Table II, but this time for the effective pure fluid using $u_{cc}(r) + v(r)$ as the sole pair interaction.

Figure 5 compares some of the functions $g(r; \beta u_{cc} + \beta v)$ (obtained by simulation with the effective colloid potential) with the original pair distribution functions $g_{cc}(r)$ of the colloid–polymer mixture. The agreement between both sets of results is quantitative.

IV. ANALYSIS OF THE EFFECTIVE POTENTIALS

We fitted the effective depletion potentials to a form inspired by the Derjaguin approximation,²⁴

$$\beta v(r) = \pi \frac{\sigma_{cc}}{2} \varphi \left(\frac{r - \sigma_{cc}}{D} - 1 \right), \quad (16)$$

where

FIG. 4. The effective depletion potential $\beta v(r)$ at the states of Table II. Symbols as in Fig. 1.

$$\begin{aligned} \varphi(x) &= a_0 x^3 + a_1^2; \quad x \leq 0, \\ \varphi(x) &= e^{-x-1} (a_3 x^3 + a_2 x^2) + a_1^2; \quad x > 0. \end{aligned} \quad (17)$$

Although a simple polynomial fit could also be used, the parameters in Eqs. (16) and (17) have simple physical interpretations: D controls the range of the interaction by setting the position of its maximum. The parameter a_0 is related to the magnitude of the depletion force “at contact” by

$$\beta F(\sigma_{cc}) = -\pi \frac{\sigma_{cc}}{2} \left(\frac{3a_0}{D} \right). \quad (18)$$

A convenient dimensionless measure of this force is given by $F^* = \sigma_{cc} \beta F(\sigma_{cc})$. The parameters a_2 and a_3 in Eq. (17) allow for a different fit beyond the maximum, but the functional form ensures the continuity of $\beta v(r)$ and its first derivative at $r = \sigma_{cc} + D$.

Figure 6 shows the dependence of $D^* = D/R_{g0}$ with the total volume fraction, $\phi = \eta_p + \eta_c$. The range of the effective depletion potential becomes smaller as ϕ is increased. We fitted D^* to the simple form,

FIG. 5. Comparison of the original radial distribution function [$g_{cc}(r)$, solid line] and the effective radial distribution function [$g(r;v(r))$, dots] at (a) state A3 and (b) state C1.

$$D^* = \frac{D_0^*}{1 + \phi/\phi_0}, \quad (19)$$

obtaining $D_0^* = 2.913 \pm 0.080$ and $\phi_0 = 0.644 \pm 0.048$. The solid line in Fig. 6 represents this fit. The parameter ϕ_0 corresponds to a characteristic volume fraction, where D^* has decreased to half of its maximum value, D_0^* . In the same

FIG. 6. The ratio of the range D to R_{g0} as a function of the total volume fraction $\phi = \eta_p + \eta_c$. The solid line is a fit to Eq. (19), and the dashed line is the reduced range for the depletion potential between two isolated hard sphere colloids as estimated in the literature (Ref. 12).

FIG. 7. The reduced force at contact $F^* = F(\sigma_{cc})/(k_B T/\sigma_{cc})$ as a function of $\phi = \eta_p + \eta_c$. The solid line is the prediction from Eq. (20), and the dashed line is the reduced force at contact for the depletion potential between two isolated hard sphere colloids as predicted in the literature (Ref. 12).

figure we show the reduced range for the depletion potential between two isolated hard sphere colloids, as calculated by Louis *et al.*¹²

In contrast to D^* , the dimensionless force at constant F^* increases with ϕ , as illustrated in Fig. 7. The parameters D_0^* and ϕ_0 just described can be used to predict F^* without further fitting. The relationship

$$F^* = \frac{(D_0^* \phi)^2}{1 + \phi/\phi_0}, \quad (20)$$

shown in Fig. 7 as a solid line, is in good agreement with the simulation data. (The reduced force for the depletion potential of Louis *et al.* for two hard spheres is also shown in that figure.) It is of interest to point out that the value $\phi_0 = 0.644$ is close to the volume fraction $\phi_{MRJ} = 0.64$ reported by Torquato *et al.* for the maximally random jammed state of spheres,²⁵ but at this point it is difficult to say whether there is a deeper connection between these quantities.

In this work we have focused on a single polymer size, $L=100$. Preliminary results of simulations of $L=300$ and $L=500$ indicate that at $L=100$ the radius of gyration already follows the scaling limit $R_g \propto L^{0.588}$ within the statistical error of our data. The sensitivity of the RDF $g_{cc}(r)$ and the effective potential to L will be investigated in the future, but it is expected to be small.

V. CONCLUSION

This work shows that accurate effective potentials can be derived for the interaction between colloids suspended in a colloid-polymer mixture. In contrast to models based on effective interactions in a binary mixture, the effective depletion potential $\beta v(r)$ considered here acts between the par-

ticles of an effective, one-component fluid of colloidal particles. The structure and phase behavior of such an effective system may be determined by conventional theoretical or simulation techniques, thereby making more tractable the original problem of determining the behavior of the full colloid-polymer mixture.

For the effective two-component model proposed by Louis *et al.*, the depletion interaction between a pair of colloids can be determined from the effective polymer-polymer and colloid-polymer potentials, either by an additional simulation of the effective mixture or by superposition approximations on the one-particle density of the colloids.¹² That formulation has the benefit that simulations of the pure polymer are sufficient to generate the necessary information. The density dependence of these potentials incorporates polymer-polymer many-body contributions to the free energy,¹¹ but colloid-colloid many-body contributions are not accounted for.

In contrast, the present calculation of the one-component effective potential by inversion of the colloid-colloid radial distribution function proceeds in a simple manner from a single colloid-polymer mixture simulation. Furthermore, since the OZ equation accounts for the simultaneous presence of more than just a pair of colloids, one can take advantage of simulations with substantial colloid densities to improve the averaging of the effective interactions and to incorporate the colloid many-body contributions directly into the effective potential.

In regard to the analysis of the depletion potentials, the usefulness of D_0^* and ϕ_0 for representing both the strength and range of $\beta v(r)$ supports their interpretation as characteristic parameters of the effective system. Their connection to the original colloid-polymer mixture will be investigated in the future.

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