Computer Simulation of Polymer-Induced Clustering of Colloids

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We have developed a novel computational scheme that allows direct numerical simulation of polymer-colloid mixtures *at constant osmotic pressure.* Using this technique, we have studied the entropic attraction that is caused by ideal polymers dissolved in a simple (hard-sphere) colloidal dispersion. In particular, we studied the nonpairwise additivity of the polymer-induced entropic interaction. The present simulations show that the nonpairwise additivity has a pronounced effect on the structure of a polymer-colloid mixture.

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The addition of a small amount of free polymer to a colloidal dispersion induces an effective attraction between the colloidal particles and may even lead to coagulation. Experimentally, this effect has been studied extensively [1] and qualitatively it is well understood [2]. The polymer-induced attraction between colloids is essentially an *entropic* effect: When the colloidal particles are close together, the total number of accessible polymer conformations is larger than when the colloidal particles are far apart. However, although this mechanism explains polymer-induced clustering *qualitatively,* a quantitative description of this phenomenon is difficult. One reason for this is that the polymer-induced attraction between the colloidal particles is not pairwise additive, particularly when the radius of the colloidal particles and the "size" of the polymers (given by its radius of gyration) are of the same order of magnitude. Moreover, the polymer-induced attraction depends both on the osmotic pressure of the polymer and on the concentration of the colloid; yet in the theoretical description of polymer-induced clustering [2], the effect of the polymer is usually replaced by an effective, density-independent, pairwise additive interaction between the colloidal particles. In order to test the range of validity of this approximation, it would clearly be desirable to carry out "exact" numerical simulations of a simple model for a colloidal dispersion in osmotic equilibrium with a polymer reservoir. Yet, even when one considers only the very simplest model, viz., that of a mixture of hard-core colloidal particles and ideal chain molecules with conformations that are restricted to a lattice, the computational problems are still formidable. What is required is a numerical scheme that samples the positions of the colloidal particles while averaging over all possible conformations of a large (and fluctuating) number of chain molecules. The "conventional" Monte Carlo schemes to simulate lattice models of polymer systems [3] would be inadequate for such a calculation.

In this Letter we show that it is possible to simulate polymer-induced attraction in a simple model for a polymer-colloid mixture, by extending a technique that was originally developed in a totally different context [4]. This approach to simulate a polymer system relies on the fact that we can recursively compute the partition function of an ideal (non-self-avoiding) lattice chain in an arbitrary external potential [5]. This is most easily seen by considering a chain of length $l-1$ on a lattice. The total number of accessible ideal chain conformations that terminate on lattice site i is denoted by $\omega_{l-1}(i)$. The total partition function of a single ideal lattice chain of length $l-1$, Ω_{l-1}, is equal to $\sum_i \omega_{l-1}(i)$, where the sum runs over all lattice sites. The total number of chain conformations of length l that terminate on site i is clearly equal to the sum of the total number of chains of length $l-1$ that terminate on any of the neighbors of i, multiplied by the Boltzmann factor associated with site i. If we assume, for convenience, that the external potential is either zero or infinite, the Boltzmann factors are just one or zero, respectively. This reasoning leads to a recursive scheme, that allows us to *exactly* compute the partition function Ω_l in an arbitrary external potential. This scheme can be used as a starting point to study self-avoiding polymers [6,7], but for the present purpose we limit ourselves to ideal polymers.

Up to this point we have not specified the nature of the external potential. We now assume that this potential is due to the presence of N hard-sphere colloidal particles, each of which occupies many lattice sites. Then the polymer partition function clearly depends on the coordinates $\mathbf{r}^N$ of the colloidal particles: $\Omega_l(\mathbf{r}^N)$. The configurational part of the partition of the system of N colloids plus one polymer of length l in volume V is then given by

$$Z(V,N,1)=\int_V d\mathbf{r}^N e^{-U_{\mathrm{hs}}(\mathbf{r}^N)}\Omega_l(\mathbf{r}^N)\,, \qquad (1)$$

where $U_{\mathrm{hs}}(\mathbf{r}^N)$ denotes the hard-sphere interaction. Here we have defined the unit of energy such that $k_BT=1$. Next, we make use of the fact that we are considering *ideal* polymers. In that case we can immediately write down the corresponding partition function for N colloids and M ideal polymers:

$$Z(V,N,M)=\int_V d\mathbf{r}^N e^{-U_{\mathrm{hs}}(\mathbf{r}^N)}[\Omega_l(\mathbf{r}^N)]^M/M!\,, \qquad (2)$$

where the factor $1/M!$ accounts for the fact that the polymers are indistinguishable. Using Eq. (2) it is straightforward to transform to an ensemble where the polymer chemical potential μ (i.e., the osmotic pressure) is kept fixed. The corresponding grand-canonical partition function is given by

$$\Xi(V,N,\mu)=\sum_{M=0}^{\infty} e^{M\mu} Z(V,N,M)/M! \\ =\int_V d\mathbf{r}^N e^{-U_{\text{hs}}(\mathbf{r}^N)} e^{z\Omega_l(\mathbf{r}^N)} . \tag{3}$$

In the last line of Eq. (3), we have introduced the polymer fugacity $z \equiv e^{\mu}$. The important point is that Eq. (3) allows us to evaluate the properties of the colloidal particles in osmotic equilibrium with a polymer reservoir. In particular it shows that we can perform Monte Carlo sampling of the colloidal particles. The presence of the polymers only affects $U_{\text{eff}}(\mathbf{r}^N)$, the effective interaction between the colloidal particles:

$$U_{\text{eff}}(\mathbf{r}^N) \equiv U_{\text{hs}}(\mathbf{r}^N) - z\Omega_l(\mathbf{r}^N) , \tag{4}$$

where $z\Omega_l(\mathbf{r}^N)$ measures the entropic interaction between the colloids due to *all* possible polymer conformations. This entropic interaction is not pairwise additive; the "many-body" part of $\Omega_l(\mathbf{r}^N)$ is due to the exclusion of polymer conformations that would have intersected three or more colloidal particles. For what follows, it is of interest to estimate how well the entropic interaction $\Omega_l(\mathbf{r}^N)$ can be approximated by a sum of pair interactions. To describe this, we write the entropic interaction $\Omega_l(\mathbf{r}^N)$ as a sum of irreducible one-, two-, three-, and many-body contributions:

$$\Omega_l^{\text{id}} - \Omega_l(\mathbf{r}^N) = \sum_i \overline{\Omega}_l^1(\mathbf{r}_i) + \sum_{\substack{\text{pairs}\\ i<j}} \overline{\Omega}_l^2(\mathbf{r}_i,\mathbf{r}_j) \\ + \sum_{\substack{\text{triplets}\\ i<j<k}} \overline{\Omega}_l^3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k) + \cdots ; \tag{5}$$

here Ω_l^{id} denotes the (ideal) polymer partition function when there are no colloidal particles present. The terms on the right-hand side of Eq. (5) are defined as follows. The one-body contribution $\overline{\Omega}_l^1$ denotes the number of polymer configurations that are excluded by one colloidal particle. This contribution is approximately constant, as it does not depend on the position of the colloidal particles, except for small variations due to the discreteness of the lattice. The two-body contribution $\overline{\Omega}_l^2$ is defined as minus the number of polymer conformations intersecting with two colloidal particles, and corrects for the fact that the one-body contribution counts these polymer conformations twice. The three-body contribution $\overline{\Omega}_l^3$ is defined as the number of polymer conformations that intersect with three colloidal particles simultaneously. The latter term corrects for the fact that the three-body contributions in the one- and two-body terms cancel exactly.

Before studying the properties of an N-body colloidal dispersion, we first consider the pure two- and three-body contributions to the entropic interaction. These can be computed directly by considering separately systems of two or three hard-sphere colloidal particles. We chose the diameter σ of the colloidal particle to be much larger than the lattice spacing ($\sigma = 10.5$, in units of lattice spacing of a simple cubic lattice). We consider both "short" ($l = 10$ lattice spacings) and "long" ($l = 50$) polymers. A measure for the size of the polymers is the radius of gyration s. For free $l = 10$ and $l = 50$ polymers these are $s_{10} \approx 1.3$ and $s_{50} \approx 2.9$, respectively. Figure 1 shows the normalized two- and three-body entropic contributions $\overline{\Omega}_*^2$ $[\equiv \overline{\Omega}_l^2/(6^l\pi\sigma^3/6)]$ and $\overline{\Omega}_*^3$ $[\equiv \overline{\Omega}_l^3/(6^l\pi\sigma^3/6)]$ for short and long polymers, as functions of the distance between the colloidal particles. Clearly, the two-body contribution yields an effective attraction between the colloidal particles. The three-body contribution $\overline{\Omega}_l^3$ is repulsive and decreases rapidly with increasing distance. For

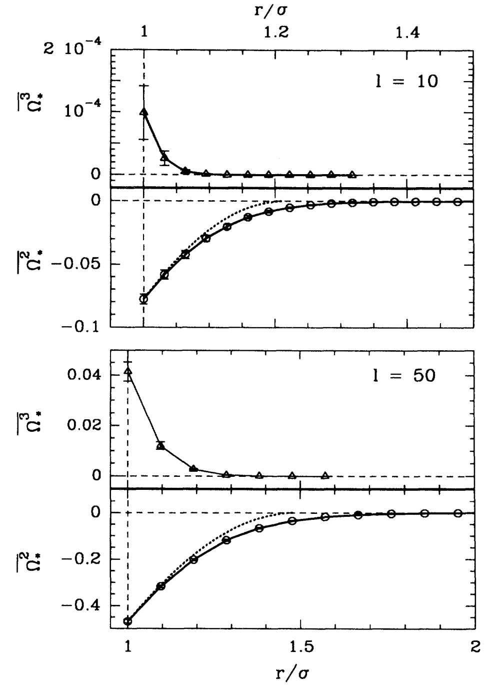

FIG. 1. Normalized two- (circles) and three-body (triangles) contributions to the polymer-induced interaction between hard-sphere colloidal particles with diameter $\sigma = 10.5$ (in units of lattice spacing of a simple cubic lattice), as functions of distance r between the colloidal particles. The two-body contribution $\overline{\Omega}_*^2$ was obtained by considering a system of two colloidal particles. The three-body contribution $\overline{\Omega}_*^3$ was obtained by considering a system of three colloidal particles in a equilateral configuration. The upper (lower) figure applies to polymers confined to a cubic lattice with length $l = 10$ ($l = 50$) lattice spacings. The error bars indicate the inaccuracy in the measured contribution. This error is a result of the discreteness of the lattice. The solid lines are drawn as a guide to the eye. The dashed line represents the theoretical result [8] for the Asakura-Oosawa model [9].

the short polymers ($l=10$) the three-body contribution is negligible, as the polymers are too short to intersect with three colloidal particles simultaneously. In contrast, the long ($l=50$) polymers give rise to a significant three-body contribution.

In the same figure, we have also indicated the theoretical prediction for the two-body contribution by Gast, Hall, and Russel [8]. This prediction is based on the Asakura-Oosawa (AS) model [9]. In the AS model both the colloidal particles and the polymers are represented by hard spheres. The colloidal spheres cannot overlap with one another or with the polymer spheres, but the latter can interpenetrate. In order to compare the numerical results for our model with those for the AS model, we have chosen the two-body contribution obtained for the AS model such that both agree at $r=\sigma$. From Fig. 1 we see that the two-body contribution obtained for the AS model agrees qualitatively with our numerical results, but has a somewhat shorter range. This is due to the fact that there is a significant number of polymer conformations that have a spatial extent larger than the diameter of the sphere representing the polymer in the AS model.

Next we consider a many-body colloidal dispersion in osmotic equilibrium with a polymer reservoir. We performed simulations for systems consisting of 108 hard-sphere colloidal particles with diameter $\sigma=10.5$, with both short ($l=10$) and long ($l=50$) polymers. The simulations were performed at constant volume and osmotic pressure, using the effective polymer-induced colloid interaction given by Eq. (4). Periodic cubic boundary conditions were used. The length of the simulation box was taken to be an integer multiple of the lattice spacing. Each simulation consisted of 10000 Monte Carlo cycles, excluding equilibration. Simulations were performed at two values of the reduced polymer fugacity: $z^*=0.01$ and 0.02. Here z^* is defined as $z^*\equiv z\times z_{\mathrm{id}}$, with $z_{\mathrm{id}}\equiv 6^l$. These values correspond to low polymer concentrations, with less than 10% of all lattice sites occupied by polymer. The density of the hard-sphere colloidal particles was 56% of regular close packing. This is some 15% below the freezing density and therefore corresponded to a typical liquid-state point. For more details about the technical aspects of the simulations, see Ref. [10].

For the mixture of colloids with short ($l=10$) polymers, we found that the local structure, as measured by the radial distribution function $g(r)$, differs only slightly from the structure of the pure hard-sphere fluid at the same density. In particular the entropic interaction induced by the polymers leads to a slight increase of $g(r)$ close to $r=\sigma$. In contrast, for mixtures of colloids with long ($l=50$) polymers, the local structure of the colloids clearly differs from the pure hard-sphere fluid. This can be seen in Fig. 2, where the radial distribution function $g(r)$ for polymer fugacities $z^*=0.01$ and 0.02 is plotted. We observe that the polymer-induced attraction leads to a strong increase of $g(r)$ for r close to σ. In addition, the second peak of $g(r)$ has also increased, and moves to lower values of r with increasing polymer fugacity.

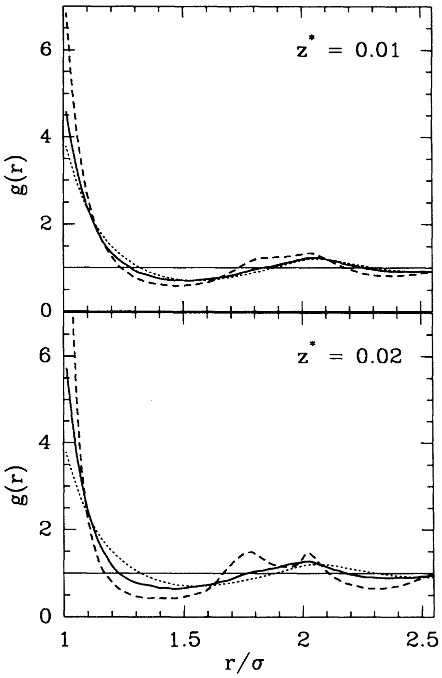

FIG. 2. Radial distribution functions of hard-sphere colloids in a mixture with long ($l=50$) polymers for polymer fugacities $z^*=0.01$ (upper part) and $z^*=0.02$ (lower part). The colloid density is 56% of regular close packing. The solid lines indicate the results obtained with the full polymer-induced many-body interaction (4). The dashed lines indicate the results obtained with the two-body approximation to the polymer-induced interaction. The dotted lines denote the hard-sphere result and serve as reference.

In order to quantify the effect of the many-body part of the effective polymer-induced interaction $z\Omega_l(\mathbf{r}^N)$ (5), we performed additional simulations in which we replaced the full polymer-induced interaction by the sum of the two-body contributions: $z\sum_{i<j}\bar{\Omega}_l^2(\mathbf{r}_i,\mathbf{r}_j)$. For the system with short ($l=10$) polymers we found that the radial distribution functions obtained with the two-body approximation and the full polymer-induced interaction exactly matches. This is to be expected, as we have seen above (see Fig. 1) that the three-body contribution is negligible for the short polymers. In contrast, the system with the long ($l=50$) polymers shows a striking difference. The radial distribution functions for the colloids obtained for this system are compared in Fig. 2, for both $z^*=0.01$ and 0.02. We observe from the figure that the two-body approximation strongly overestimates the polymer-induced attraction. At $z^*=0.02$ the second peak in $g(r)$ has even split, indicating a drastic but spurious change in the local structure of the colloids. Apparently the three-body contribution, which acts as a repulsive force at short distances, has a significant effect on the lo-

cal structure. This result shows that the two-body contributions alone fail to describe the local structure of colloidal systems in osmotic equilibrium with long polymers.

In conclusion, we have developed an efficient method that allows us to simulate a simple model for polymer-colloid mixtures under the "experimental" condition of constant osmotic pressure. We computed the two- and three-body contributions to the polymer-induced entropic interaction between hard-sphere colloidal particles. For long polymers, we have found that taking into account only the two-body contributions leads to a strong overestimation of the tendency of the colloid to cluster, even at relative low polymer concentrations. These results suggest that there is a need to reconsider the theoretical descriptions of polymer-induced clustering in colloidal dispersions.

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