

One-dimensional Diffusion of Colloids in Colloid-Polymer Mixtures

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Introduction

Colloid-polymer mixtures serve as model systems to study complex fluids. The challenge in this study lies in the fact that these are systems where the relevant physical processes often occur over a wide range of characteristic length and time scales which can be strongly correlated. The addition of soluble non-adsorbing polymer to colloidal dispersions, even in small amounts, has a significant effect on transport properties (mainly because it induces a new type of interaction between colloidal particles, the depletion interaction).

When non-adsorbing polymers are added to a suspension of hard-sphere-like colloidal particles, an effective, generally attractive interaction is induced between the colloidal particles. The origin of this interaction is the depletion effect: the exclusion of polymer from the depletion zone between the colloids give rise to an unbalanced osmotic pressure. Alternatively, one can view the depletion induced attraction as arising from an increase in the entropy of the polymers.

When colloid-polymer systems are confined by surfaces, boundary and wall effects become important. Diffusion in quasi one-dimensional geometries is of particular interest not only because of practical applications for diffusion processes in microporous solids^{1,2} and in biological channels³⁻⁵ but also because of the emergence of a new regime (anomalous diffusion) in the long-time dynamics of colloids.

Description of the model

Consider a mixture of colloids and polymers in a solvent confined in a cylindrical channel. In the Asakura-Oosawa model, colloid-colloid and colloid-polymer interactions are just hard-core repulsions whereas polymers are considered as ideal interpenetrating coils. Furthermore, colloids cannot pass each other if the channel is narrow enough (single-file diffusion), and their motion will effectively be restricted to translations along the central axis of the channel. On the other hand, depending on its size and the ability to pass the colloids, a polymer can be regarded as a one-dimensional rod of length $2R_g$ or as a three-dimensional sphere of radius R_g . In both cases, the binary mixture can be reduced (at least from thermodynamics point of view) to an effective one-component system with a modified Hamiltonian, by integrating out the polymer degrees of freedom and neglecting three- and higher-body potentials. This reduction is exact for polymer to colloid size ratios which are less than one ($q=\sigma_p/\sigma_c<1$).

In order to calculate the diffusion coefficients, it is necessary to specify the microscopic diffusivity tensor D_{ij} . Screening of hydrodynamic interactions in quasi-one-dimension allows us to restrict ourselves to the pair-wise part of the hydrodynamic interactions. At this level, expressions have recently been developed^{6,7} for the elements of the diffusivity tensor that take the finite size of the Brownian particles into account. In the present treatment, the hydrodynamic coupling between the motions of polymers and colloids will be neglected. Therefore, apart from the direct interactions, polymers affect the motion of colloids by changing the viscosity of the solvent. In other words, they provide an effective medium for the colloids.

Short-time diffusion

For time intervals shorter than the time between particle collisions, the mean-squared displacement of colloids in a randomizing background fluid is proportional to time. The proportionality constant identifies the short-time self-diffusion coefficient D_s^s .

D_s^s is then obtained by averaging of D_{11} in the canonical ensemble, which requires the knowledge of the colloid-colloid pair distribution function $g(x)$

$$\frac{D_s^s(\eta)}{D_0} = 1 + \chi_w + \frac{\eta}{\beta} \int_0^\infty d\xi g(\xi) \chi_p(\xi)$$

In the above expression, η is the packing fraction of colloids, β is ratio of colloid to channel radius, and χ_w and χ_p represent the hydrodynamic effect of the walls and of the other colloids, respectively. The assembly of colloidal particles, within our model, is equivalent to a one-dimensional fluid of hard spheres (rods) with nearest-neighbor interactions. For these types of systems, there is a systematic method to find $g(x)$ ⁸. However, exact analytic closed-form expressions, even for linear potentials, are only feasible for short separations⁹. An alternate way of getting “exact” results for $g(x)$ is via Monte Carlo simulations.

Long-time diffusion

Excluding the mutual passage of colloids forces them into a single file with a fixed spatial sequence, and severely restricts the probability for large particle displacements, thereby drastically reduces the diffusion rate at long times. The mean-squared displacement is no longer proportional to time but to the square root of time. Strictly speaking, the diffusion coefficient is zero. Nevertheless one can define the mobility factor, F , as the rate of transport through the following relation

$$\langle x^2(t) \rangle = 2Ft^{1/2} \quad ,$$

It has been shown that for particles with short-range interaction, the mobility factor depends on the short-time collective dynamics of the system, and in the hydrodynamic limit it is given by

$$F(q) = \frac{S(q)}{\rho} \sqrt{\frac{D_c^s(q)}{\pi}}$$

$S(q)$ and $D_c^s(q)$ are the static structure factor and short-time collective diffusion coefficients of colloids at wavenumber q , respectively, and ρ is the colloid number density. Within the framework of Smoluchowski dynamics, the short-time wavenumber-dependent collective diffusion coefficient can be written as

$$D_{eff}(q) = D_0 \frac{H(q)}{S(q)} \quad ,$$

where $H(q)$ is the hydrodynamic function.

Results and discussion

For channels with a diameter of a few microns and with polymers that can pass the colloids the three-dimensional model of a polymer is an appropriate model. Adopting this model, the pair distribution function of colloids can be obtained from Monte Carlo simulations. Fig.1 shows $g(r)$ for two selected values of η_c . Comparing with the pair distribution function of pure colloids reveals that the depletion interaction leads to a higher value of $g(\sigma_c)$, as expected.

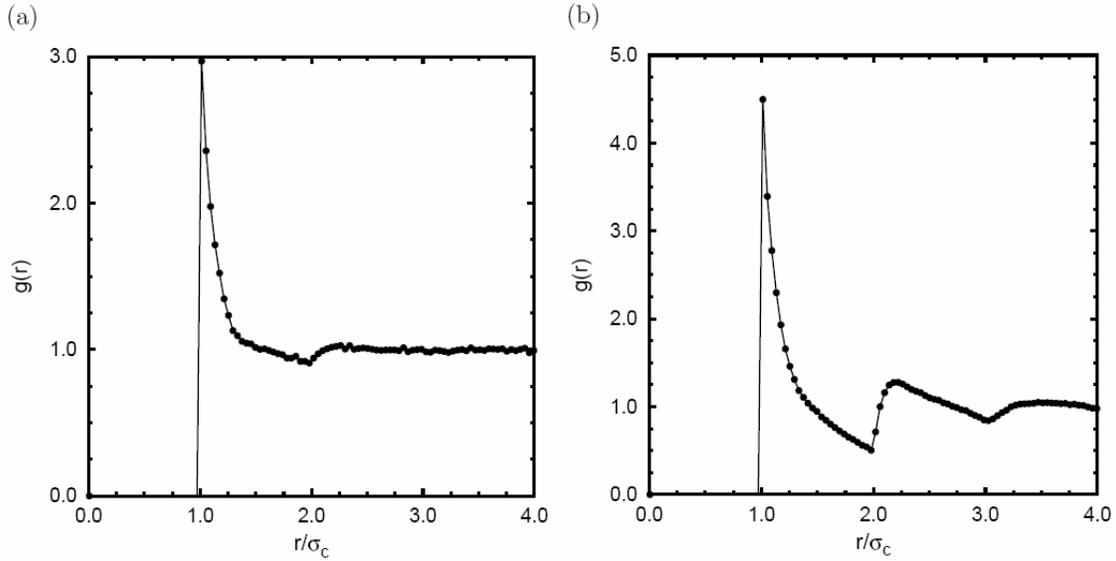


Fig.1: Radial distribution function of colloids in a colloid-polymer mixture for $\eta_p = 0.2$ and $q = \sigma_c/\sigma_p = 0.4$; (a) $\eta_c = 0.2$. (b) $\eta_c = 0.6$.

The reduction of the self-diffusion coefficient upon addition of polymers to the solution is depicted in Fig.2. It is customary to write the diffusion coefficient in terms of a virial expansion in density or volume fraction. The second virial coefficient is negative in our case, in contrast to the case of diffusion of colloids in bulk solutions.

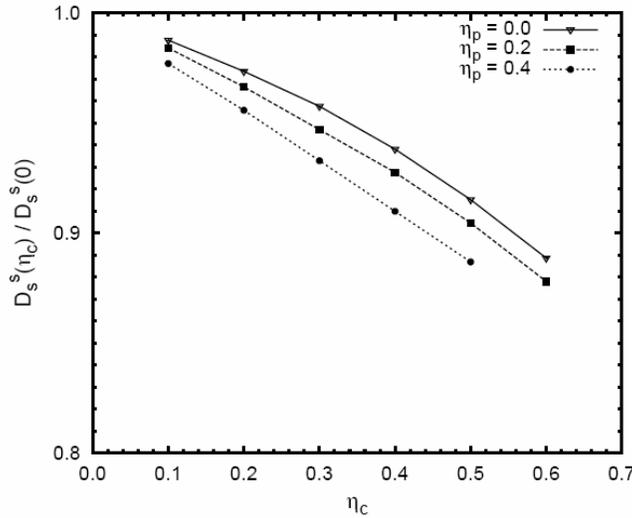


Fig.2: Short-time self-diffusion coefficient of colloids in solution with and without polymer $\beta = a/R = 0.216$ and $q = 0.4$.

Next, the short-time collective diffusion coefficient and long-time mobility factor of colloids in a colloid-polymer mixture are determined. Fig.3 exhibits an interesting feature of D_c^s , namely its growth with concentration. It also shows that the addition of polymer reduces the cooperative diffusion of colloids, in accord with intuition.

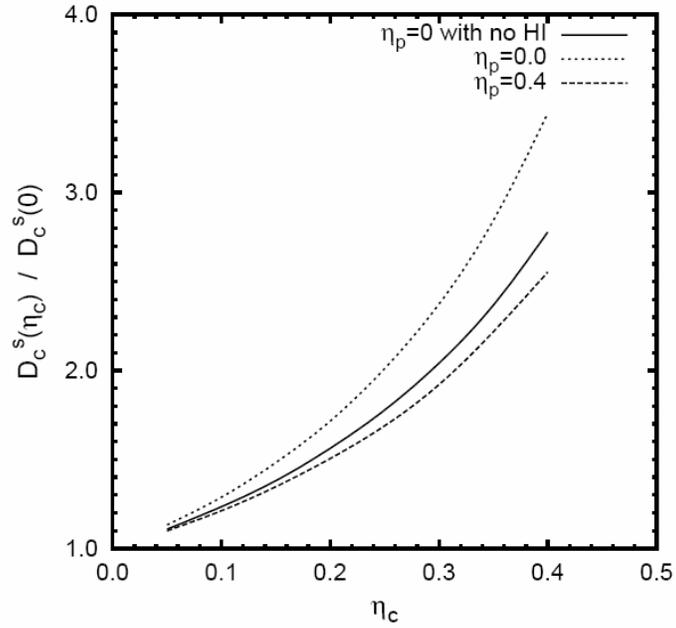


Fig.3: Short-time (macroscopic) collective diffusion coefficient of colloids in solution with and without polymer. The case where hydrodynamic interactions (HI) are absent is also plotted for reference.
 $\beta = a/R = 0.216$ and $q = 0.4$.

In contrast to the collective diffusion coefficient, the long-time mobility factor is enhanced in systems with short-range attractive interactions in one dimension compared to systems where hard-core repulsive forces are the only source of direct interactions (Fig.4).

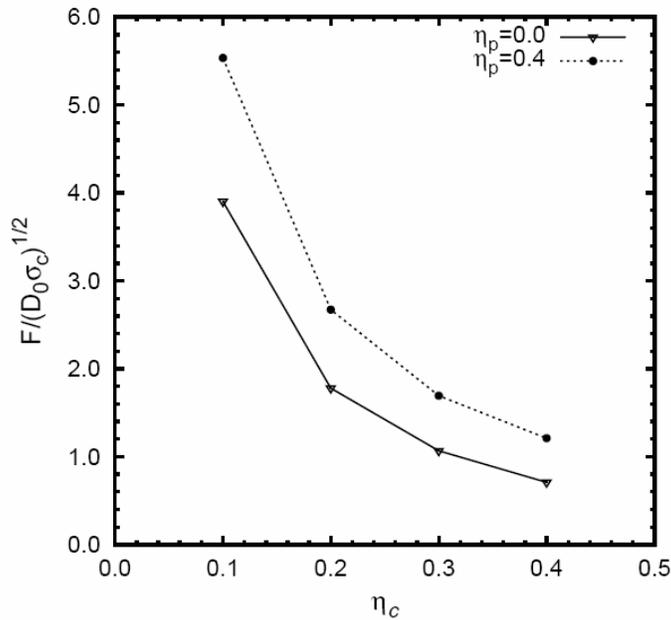


Fig.4: Long-time mobility factor of colloids in solutions with and without polymer.
 $\beta = a/R = 0.216$ and $q = 0.4$.

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