



Depletion and the dynamics in colloid–polymer mixtures



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ABSTRACT

The status of work on the influence of nonadsorbing polymers on depletion dynamics in colloidal dispersions is reviewed. In the past focus has been paid to equilibrium properties of colloid–polymer mixtures. In practice the dynamical behaviour is equally important. Dynamic properties including colloid diffusion, sedimentation and suspension rheology as affected by polymer-induced depletion attraction are discussed.

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1. Introduction

Colloid–polymer mixtures have gained increasing attention since the 1980s for both practical and fundamental reasons. In many industrial products such as food [1], and paint [2], polymers and colloids are mixed together so studies on colloid–polymer mixtures are very helpful for giving insight into for instance the conditions that keep the mixtures stable. Fundamentally, it is understood that adding nonadsorbing polymers to a colloidal dispersion allows tuning the range and strength of the attractive pair interactions and alters the colligative properties of colloidal mixtures. In practice however the nonequilibrium behaviour is at least as important. In this review we focus on the dynamics of relatively dilute and stable colloidal dispersions.

In contrast to equilibrium properties of colloid–polymer mixtures set by thermodynamics [3], there are relatively few investigations on dynamics that couples Brownian motion, hydrodynamic interaction, polymer transport and microstructure evolution in colloid–polymer mixtures. Dynamical properties such as diffusion, sedimentation, and suspension rheology have been studied in well-defined colloidal (hard-sphere and adhesive hard-sphere) suspensions in great detail

[4–6], and these are highly relevant for understanding suspensions containing colloidal particles plus nonadsorbing polymers. Phase transition phenomena have drawn quite some attention [7,8]. The demixing process of an unstable colloid–polymer mixture can proceed in several ways. Both spinodal decomposition [9–11] as well as nucleation and growth coarsening can take place.

Before reviewing the dynamics, the key aspects of equilibrium properties in colloid–polymer mixtures are briefly summarized. Adding non-adsorbing polymers to a dispersion of colloidal spheres effectively induces attractive forces between them [3]. The attraction originates from the presence of depletion zones around the colloidal spheres, each having a volume $v_c = 4\pi a^3/3$, with sphere radius a . The depletion zone results from a loss of conformational entropy of the polymer chains close to the surface of the colloidal particles. Overlap of depletion zones causes an inhomogeneous osmotic pressure distribution by the polymers around the neighbouring particles, first understood by Asakura and Oosawa [12]. The Asakura–Oosawa–Vrij (AOV) expression for the depletion interaction [12,13] between two colloidal hard spheres, each surrounded by a depletion layer with thickness δ is:

$$W(r) = \begin{cases} \infty & r < 2a \\ -\Pi V_{ov}(r) & 2a \leq r \leq 2(a + \delta) \\ 0 & r > 2(a + \delta) \end{cases} \quad (1)$$

The osmotic pressure of the polymer solution Π depends on the polymer concentration c and can, for ideal (non-self-interacting) depletants, be written as $\Pi v_c q^3/kT = c/c^*$ in the case of a dilute polymer

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solution, where $q = \delta/a$ and c^* is the polymer overlap concentration. The interparticle dependent overlap volume of depletion layers,

$$V_{ov}(r) = \frac{4\pi}{3} (a + \delta)^3 \left[1 - \frac{3}{4} \frac{r}{a + \delta} + \frac{1}{16} \left(\frac{r}{a + \delta} \right)^3 \right],$$

is a function of the size of the polymers in solution [13]. The minimum value of the potential appears at $r = 2a$, where $W(r = 2a)/kT = (1 + 3a/2\delta)c/c^*$.

Hence the resulting attractive interaction can be tuned by polymer size and concentration. In the last few decades research on depletion forces focused on equilibrium aspects of colloid–polymer mixtures: the depletion interaction, phase behaviour, and scattering properties were primary focus areas [3]. A key quantity that influences colligative properties such as osmotic pressure, phase stability, diffusion and sedimentation is the second osmotic virial coefficient B_2 , defined as

$$B_2^* = 12 \int_0^\infty \left(1 - \exp \left[-\frac{W(r^*)}{kT} \right] \right) r^{*2} dr^*, \quad (2)$$

where $r^* = r/2a$ and $B_2^* = B_2/v_c$.

Next we review polymer-depletion induced dynamics in colloid–polymer mixtures and challenges encountered in systematic studies. The discussion starts in Section 2 with a relatively simple case of unidirectional flow of a polymer solution next to a planar nonadsorbing wall. Then the subject is shifted towards the effect of a depletion layer on the friction experienced by a single sphere in Section 3, followed by the dynamics of two interacting particles in Section 4. The volume fraction dependence of the diffusion coefficient, sedimentation and viscosity as mediated by depletion effect is discussed subsequently in Sections 5, 6 and 7 and this paper ends with concluding remarks.

2. Polymer depletion dynamics at a wall and in a slit

When a solution containing nonadsorbing polymers is sheared next to a planar wall at constant shear stress, both the shear rate and viscosity depend on the position from the wall surface. Once the viscosity profile is determined, the (apparent) slip velocity and slip (or Navier) length b can be derived. It has been shown [14] that the viscosity follows the segment density profile. The equilibrium segment density profile near a single planar wall reads [15] $\rho(x) \approx \tanh^2(x/\delta)$, with the depletion thickness δ characterizing the length scale over which polymer chains are depleted from the wall; $\rho = 0$ at the wall ($x = 0$) and $\rho = 1$ in the bulk ($x \rightarrow \infty$). For a dilute polymer solution at a planar wall an analytical expression for the slip length was obtained [14]:

$$b = \delta \left(\frac{\eta_p}{\eta_0} - 1 \right) \approx \delta \sqrt{[\eta] c_b} \tan^{-1} \left(\sqrt{[\eta] c_b} \right). \quad (3)$$

This result describes the slip measured with computer simulations with ideal polymers [16] quite well. An analytical expression for b for polymer chains with excluded volume interactions can also be obtained [17]. In practice, these results are relevant to predicting fluid flow with dissolved or dispersed polymers, micelles or colloids through pipes, in interpreting measurements of the viscosity of a colloidal dispersion or polymer solution using capillary rheometry [18], pore flow [19] or using polymer solutions to sweep out oil out of natural porous media.

Taniguchi et al. [20] theoretically investigated the fluid flow of a nonadsorbing polymer solution across a slit. It was assumed that the walls of the infinitely long slit are permeable to solvent only. The work revealed non-equilibrium polymer segment concentration profiles distorted by convection for a given solvent condition, polymer size and concentration, and slit width, see the schematic illustration in Fig. 1. Extending this nonequilibrium model to higher dimension flow fields is challenging.

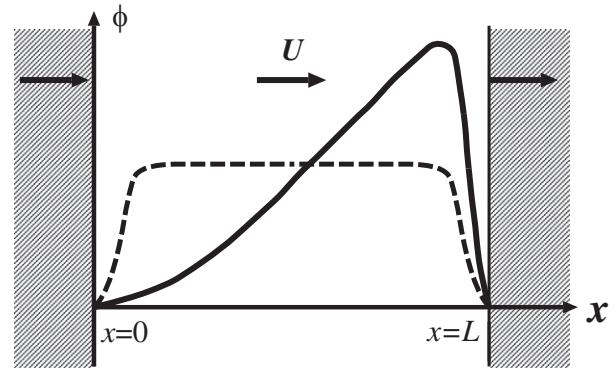


Fig. 1. Illustration of the convective depletion effect on the polymer segment concentration profile between two nonadsorbing parallel walls that are permeable for solvent. The solvent flow goes from left to right. For small flow rates of solvent through the walls the polymer segment concentration attains the (symmetric) equilibrium profiles (dashed curve). For higher flow rates the polymer concentration profiles get distorted and become asymmetric (solid curve).

Flow around a sphere mediated by the depletion effect is considered next for it is important for estimating transport properties such as diffusion [21] or sedimentation [22] of colloidal particles and proteins through a solution containing macromolecules. This is related to the long-time or zero-frequency limit in microrheology [23], and diffusing wave spectroscopy measurements [24], for which it is essential to understand the flow induced by a colloid through a complex medium filled with polymer chains.

3. Motion of a sphere through a polymer solution

Brownian motion of a colloidal particle in a solvent originates from the stochastic bombardment with solvent molecules. The kinetic energy of a colloidal particle gained from thermal fluctuations is dissipated due to hydrodynamic friction. The typical Brownian time scale t_B is approximately $m/6\pi\eta_0 a$, with particle mass m and solvent viscosity η_0 . At time scale $t \gg t_B$ the translational frictional coefficient $6\pi\eta_0 a$ can be obtained by linear Stokes flow around the spherical particle. As a colloidal sphere moves through a polymer solution it ‘senses’ a fluid with non-uniform viscosity, resulting in an effective viscosity that the sphere experiences. This effective viscosity identifies how strongly sphere motion is retarded. Since the 1980s studies have been performed on dilute spheres translating through a polymer solution, see for instance refs [22,25–29], using experimental techniques such as dynamic light scattering, NMR, electrophoresis and sedimentation. The translational friction coefficient is often interpreted in terms of the Stokes approximation in a polymer solution $6\pi\eta_p a$, where η_p is the viscosity of the polymer solution. The obtained effective viscosity η_{eff} that follows from the measured diffusion coefficient $D_\delta = kT/6\pi\eta_{eff} a$ lies, however, in between the values for the viscosity of a pure solvent η_0 and of the bulk polymer solution, η_p , implying a slip-like behaviour at the particle surface.

Fan et al. [30] derived analytical results for the effective viscosity a sphere experiences by including the depletion layer via a simplified two-layer approximation for both the translational and rotational motion. The results depend on depletion thickness, sphere radius and the solvent and polymer bulk solution viscosity, and have been compared to an asymptotic model and numerical results [31], where a continuous viscosity profile is fully accounted for (see data points in Fig. 2).

For $\delta/a < 0.3$, the two-layer approximation is very accurate. For depletion thickness significant deviations occur, especially if δ gets

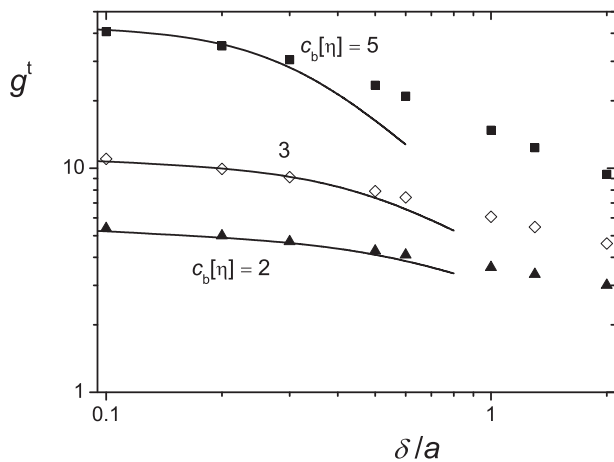


Fig. 2. Correction function to the translational friction coefficient $g^\dagger = \eta_{\text{eff}}/\eta_0$ as a function of the relative depletion thickness δ/a for three polymer concentrations as indicated. Data: numerical results obtained using the full depletion and hence viscosity profiles around the sphere from [31]. Solid curves follow the analytical two-layer results [30].

close to a . In the limit of a thin depletion layer the asymptotic slip length b that follows from the two-layer model [30] is

$$b = \delta \left(\frac{\eta_p}{\eta_0} - 1 \right) \left(1 - 3 \frac{\delta}{a} + \dots \right). \quad (4)$$

Apart from the first-order curvature correction term, $-3\delta/a$, this result is identical to Eq. (3). The depletion layer results in slip so that the sphere experiences an effective viscosity that is smaller than the bulk viscosity. For rotational motion the slip effects are more pronounced [30]; when a sphere rotates it mainly drives the nearby fluid within the depletion layer around the sphere.

For the semi-dilute polymer concentration regime, the transport coefficients are often used in semi-empirical correlations, discussed for instance by Odijk [32]. Tuinier and Fan [33] rationalized these relations using the theoretical approach by Fan et al. [31], providing theoretical values for the scaling parameters under the assumption that the depletion zones are not distorted for long-time self-diffusion. As mentioned above, when fluid flow strongly interacts with depletion, the polymer segment distribution is no longer in equilibrium. Such convective depletion effect was first discussed by Odijk [34] who described a thin depletion boundary layer in front of a fast moving sphere.

In order to understand the short-time behaviour Ochab-Marcinek et al. [35] presented a theoretical description of momentum relaxation based on an assumption that the random motion of a surrounding depletion envelope and sphere itself are independent. This ‘walking’ confined diffusion model is different from anomalous diffusion [36] but experimental data generated from this model have features of anomalous diffusion. Dynamic light scattering and fluorescence correlation spectroscopy experiments on various dilute suspensions of colloidal spheres plus nonadsorbing polymers could be described quite well using this model [35,37].

4. Dynamics of two spheres in a polymer solution

Vliegenthart and van der Schoot [38] investigated the time evolution of the depletion potential between two spheres using Brownian dynamics simulations and scaling theory. Their results imply that the instantaneous potential should be handled with care in kinetic studies. Krüger and Rauscher [39] investigated the nonequilibrium fluid structure mediated forces between two colloids driven through a suspension of mutually noninteracting Brownian particles. They found an enhancement of the friction experienced compared to the friction an isolated particle feels for two colloids driven side by side. Under the assumption

of instantaneously formed depletion layers the hydrodynamic interaction between two colloids mediated by non-adsorbing polymer chains were considered for two colloidal hard spheres moving along their centre-to-centre line [40]. The resulting effective viscosity asymptotically approaches the single sphere limit for large interparticle distances. As the particles get closer the effective viscosity decreases and finally approaches the lubrication limit, where the friction equals that of two close-approached spheres in a pure solvent. The flow analysis shows that the circulation pattern, a characteristic for the presence of the depletion layer, expands upon approach of the particles, see Fig. 3.

Karzar-Jeddi et al. [41] theoretically studied the stochastic interactions of a pair of Brownian hard spheres in a nonadsorbing polymer solution, including a complete pair mobility analysis. The hard spheres were hypothetically trapped by optical tweezers and allowed for random motion near the trapped positions. The polymer solution was simplified by a two-layer solvent; layers with a solvent viscosity η_0 surrounding the spheres and a bulk with a polymer solution viscosity η_p . From the mobility analysis it followed that the presence of depletion layers around the hard spheres affects the hydrodynamic interactions and particle dynamics as compared to the pure solvent and uniform polymer solution cases. The reduction of the viscosity in the depletion layers around the spheres and the entropic force due to the overlapping of depletion zones have a significant influence on the auto- and cross-correlated Brownian interactions. This method offers the possibility to effectively simulate the dynamic properties of a collection of spheres plus depletants. Below the focus shifts towards the colligative dynamic properties of colloidal spheres mixed with nonadsorbing polymers.

5. Concentration-dependant diffusion

In this section the volume fraction dependence of diffusion of spheres through a polymer solution is considered. The influence of an attractive potential on the diffusivity was investigated theoretically based on sticky spheres [42] or using an effective direct attraction [43], and experimentally using dynamic light scattering [11,42]. However, a theoretical description of the diffusion processes in colloidal suspensions with interacting particles in the presence of nonadsorbing polymers is not yet available. Beyond the dilute limit the diffusion process becomes dependent on the experimental length scale. In the limit where the ‘size’ of the concentration fluctuation of colloidal particles is sufficiently larger than a particle diameter, the particles undergo a collective diffusion on a time scale $t \gg t_B$. Collective diffusion (CD) is a process during which concentration gradients gradually disappear due to Brownian motion of the particles. When focusing on a smaller length scale than that of the concentration fluctuation, the motion of a tagged colloidal particle is monitored and self-diffusion is observed. Self-diffusion (SD) refers to the Brownian motion of a tagged particle in a dispersion. In scattering experiments, where the relevant length scale regime is set by the inverse of the scattering wave vector Q , one may distinguish collective diffusion at small $Qa \rightarrow 0$ from self-diffusion at $Qa \gg 1$. One may further sequester short-time and long-time self-diffusion [44]. If one would label a small fraction of particles and only study their SD behaviour this corresponds to long-time self-diffusion. When measuring the averaged diffusion coefficients of all particles the short-time behaviour is attained.

Theoretical understanding of the dynamics of concentrated colloid-polymer mixtures remains a great challenge. A promising approach is the combination of the two-fluid model and the dynamic self-consistent field theory [20]. This has been applied to describe flow of a polymer solution through a slit and allows computing the deformation of the polymer depletion zones as mediated by fluid flow. The calculation of physical properties at higher dimensional flow profiles and many particles is however quite expensive computationally, even at the mean-field level.

At present most theories for CD and SD were derived for (adhesive) hard spheres. Since the polymers induce an effective attraction it is

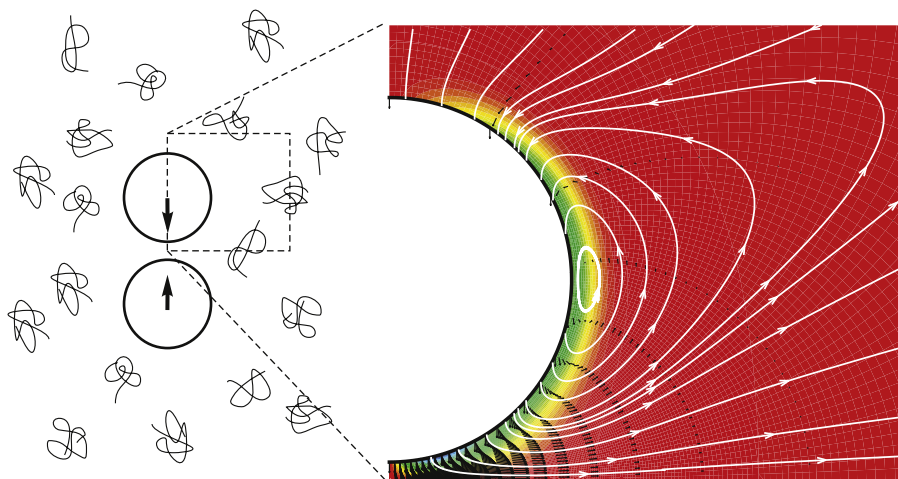


Fig. 3. Flow and vorticity patterns in a nonadsorbing polymer solution near a hard sphere close to another hard sphere. Polymer segment concentration profiles are approximated as mean-field equilibrium profiles.

interesting to compare the influence of polymer-mediated attraction with those of sticky hard spheres, spheres with short-ranged attractions, of which the diffusion has been studied experimentally [45]. The sticky sphere model of Baxter [46] for particles interacting via an extremely short-ranged attraction can be employed providing simple expressions for the second osmotic virial coefficient and the equation of state. In the Baxter model the stickiness parameter τ plays the role of an effective temperature. For $1/\tau = 0$ the sticky spheres are hard. The effective temperature or stickiness parameter τ is connected to B_2^* via

$$B_2^* = 4 - \frac{1}{\tau}. \quad (5)$$

This allows to link any short-ranged attraction to τ by connecting Eqs. (2) to (5). One possibility to connect short-ranged depletion forces to the τ parameter is via Cichocki and Felderhof's expressions [47] for diffusivities of adhesive hard spheres. Specifically, the lowest order volume fraction dependence of the collective diffusion coefficient is:

$$\frac{D}{D_0} = 1 + (1.454 - 1.125/\tau)\phi, \quad (6)$$

whereas for self-diffusion the results are

$$\frac{D}{D_0} = \begin{cases} 1 - (1.8315 + 0.295/\tau)\phi & \text{short} \\ 1 - (2.0972 + 0.562/\tau)\phi & \text{long} \end{cases} \quad (7)$$

Here the diffusion coefficient of a single hard sphere through a pure solvent is denoted by D_0 , and in a polymer solution D_0' . The results summarized in Eqs. (6) and (7) might well hold in general for spherical particles with a hard core and a short-ranged attraction. For these SD and CD processes it is clear that attractions slow down particle motion in dilute dispersions. The attractive interactions tend to induce transient clusters because the probability that two particles are close to each other is larger for sticky spheres as for hard spheres. This leads to additional hydrodynamic interaction which increases the effective friction, hence slows down diffusion. For dilute sticky silica spheres this expression could quantitatively describe measured short-time self-diffusion coefficients [45]. CD of spherical particles in a colloid-polymer mixture has been measured by Ramakrishnan et al. [48]. Bodnár et al. [42] studied the Q -dependent collective diffusion coefficient of hard-sphere like silica particles in a solution of nonadsorbing PDMS polymers in cyclohexane near the spinodal curve. In these studies it was shown that depletion-induced attractions slow down self-diffusion tremendously. The theoretical results for diffusion coefficients of hard and

sticky hard spheres have been verified also for more practical situations. In a seminal paper, de Kruif [49] verified that the self- and collective-diffusion coefficients of casein micelles in skim milk can be accurately described using Eqs. (6) and (7) for $1/\tau = 0$ and that removing the stabilizing brush layer of casein micelles (making them attractive and induces gelation for cheese-making), which makes them attractive, modifies the diffusion coefficient in line with Eqs. (6) and (7) for finite τ .

Since for sticky spheres the influence of the direct attraction is known, see Eqs. (6) and (7), this might also hold for depletion interactions. It should be realized that the depletion interaction arises indirectly as a result of the direct interactions between hard spheres and polymer chains, the direct interactions between hard spheres and the interactions between the polymer chains. One can debate whether this effective interaction alone suffices to describe the dynamics of colloid-polymer mixtures. If that would be correct it means one is allowed replacing a mixture of hard spheres and polymers with an effective one component fluid; a mixture of spheres interacting through a depletion potential. For the equilibrium properties, Dijkstra et al. [50] showed that this is only correct for hard spheres mixed with polymers when $\delta < 0.15a$. Juárez-Maldonado and Medina-Noyola [51] demonstrated that the presence of the polymers as separate component strongly influences the dynamics for a dense colloidal suspension. This result implies that the above effective one-component approach might not suffice to describe the dynamics of colloidal particles. The coupling of competing effects of osmotic, hydrodynamic resistance and depletion induced slip-like behaviours needs to be investigated thoroughly by a combined systematic experimental, theoretical and preferably, coarse-grained many particle Brownian simulation approach.

6. Sedimentation and creaming

The sedimentation velocity of a single sphere in a solvent follows from the balance of Stokes friction and the gravitational and buoyant forces as $U_0 = 2a^2g\Delta\rho/(9\eta_0)$, where $\Delta\rho$ is the density difference between particle and solvent. For a single sphere sedimenting through a nonadsorbing polymer solution, $U_0' = U_0'\eta_0/\eta_{\text{eff}}$. The general expression for the ensemble-averaged sedimentation velocity $\langle U \rangle$ of a dilute particle suspension in a pure solvent to the lowest order in volume fraction was derived by Batchelor [52]. For sticky spheres the expression becomes [53]

$$\frac{\langle U \rangle}{U_0'} = 1 - (6.55 - 0.88/\tau)\phi. \quad (8)$$

For sticky silica spheres this result has been confirmed experimentally [53]. Moncho-Jordá et al. [54] performed mesoscopic computer simulations on spherical particles including hydrodynamic interactions and verified that Eq. (8) holds up to about $\phi \approx 0.03$ for various strengths of the short-ranged attraction giving various values for the stickiness parameter τ . Up to at least $\phi \approx 0.13$ the qualitative influence of attractions on the sedimentation velocity remains similar: increasing attraction enhances the sedimentation speed.

Whitmer and Luijten [55] examined the interplay of colloidal attractions and gravitational force in determining the structure of particle sediments. They showed that for weak attractions between the spheres, too low to induce cluster formation during sedimentation, the density profiles of the colloidal sediment are similar to those at equilibrium. For stronger attractions, dense colloidal clusters form during sedimentation, which settle into loosely packed, disordered structures. Tong et al. [22] measured the sedimentation of small calcium carbonate particles stabilized with surfactant through a solution containing polyethylene propylene (PEP) polymers in decane. Interpretation of the measured data was involved. The creaming of emulsion droplets in a solution containing nonadsorbing polysaccharides has been measured by Tuinier and de Kruijff [56]. They describe the creaming rate by using a semi-empirical generalized Stokes–Einstein equation for sedimentation. A theoretical prediction for the creaming rate, however, remains a challenging problem.

7. Rheology

Systematic studies on the rheology of colloidal dispersions plus nonadsorbing polymers are quite limited. The experimental investigations of rheological properties were mainly related to fractal aggregates formed [57–60], mainly to relate this to and study fractal aggregation. In practice it is important to understand the interplay of rheology modification with the attractive depletion force by adding polymers to a colloidal suspension. This is not at all clear yet. Insights were obtained when looking at the shear viscosity of sticky Baxter spheres for which Cichocki and Felderhof [47] derived the low volume fraction result in the limit of small Peclet numbers:

$$\frac{\eta}{\eta_0} = 1 + \frac{5}{2}\phi + (5.913 + 1.899/\tau)\phi^2, \quad (9)$$

where η_0 is the effective viscosity experienced by a single sphere. The rheology of sticky spheres and a mixture of bidisperse hard spheres were studied experimentally [61,62] with the shear viscosity described by Eq. (9). Near the critical gas–liquid point of a colloid–polymer mixture the viscosity diverges in line with Eq. (9) [63]. A review of semi-empirical relations between the shear modulus and the pair interaction and the visco-elasticity of colloid–polymer mixtures can be found in Quemada [64] and Meller et al. [65].

8. Concluding remarks

Recent developments that have led to better understanding of polymer–depletion mediated dynamical properties are reviewed. For the single particle case the presence of a polymer depletion zone leads to an effective slip. In the presence of a second particle the slip effects are enhanced. This implies that measurements of equilibrium properties such as the measurement of interparticle force using optical tweezer contains information on both pair interactions and (hydro)dynamics. The colligative dynamic properties of a collection of colloidal particles including diffusion, sedimentation and suspension viscosity and the influence of nonadsorbing polymers are discussed. Illustrative experimental works and limited theoretical approaches are outlined. The needs and plenty of opportunities are indicated for both experimental and theoretical systematic investigations.

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