

Sedimentation of Colloidal Particles through a Polymer Solution

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We report sedimentation measurements of small colloidal particles through a nonadsorbing polymer solution. The experiment reveals that the particles “feel” the single-chain viscosity rather than the solvent viscosity when their radius R_c is smaller than the correlation length ξ of the polymer solution. The particles experience the macroscopic viscosity of the polymer solution when $R_c \gg \xi$. In the transition region, the particle’s friction coefficient does not have the predicted scaling form. Instead, a new switch function is found to be of universal form independent of the polymer molecular weight. [S0031-9007(97)04099-4]

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The study of transport of macromolecules in a spatially inhomogeneous medium, such as a polymer gel and a porous medium, is of fundamental interest in statistical physics and it is also relevant to many technological and biological processes involving separating or removing polymer molecules, proteins, and other large biomolecules. Examples include chromatography, catalysis, and electrophoresis. In these processes one is interested in the translational mobility of the macromolecules under the influence of an external field through a medium with complex spatial structures [1]. To understand the basic principles governing the transport phenomenon, we consider a simple case of sedimentation of a dilute suspension of colloidal particles through a nonadsorbing polymer solution, in which the polymer chains form a fluctuating network [2]. The main issue in colloidal sedimentation is to understand how particle-polymer and polymer-polymer interactions affect the frictional force experienced by the particles [3]. The frictional force can be expressed by the normalized friction coefficient $F_c \equiv \eta_c/\eta_0$, which is the ratio of the microscopic viscosity η_c experienced by the particles in the polymer solution to the solvent viscosity η_0 . Many years ago de Gennes and his co-workers [2,4] proposed that when the particle radius R_c is smaller than the correlation length ξ , which describes the average mesh size of the fluctuating polymer network, the particles move easily and they only “feel” the solvent viscosity η_0 , i.e., $F_c = 1$. When $R_c \gg \xi$, the particles are trapped and their friction coefficient is given by $F_c = \eta_p/\eta_0$, where η_p is the macroscopic viscosity of the entangled polymer solution. In the transition region, F_c is expected to be a scaling function $\varphi(R_c/\xi)$, which depends only on the polymer concentration C_p and is independent of the polymer molecular weight M_p . (Hereafter, we will use the subscripts c and p to refer to the colloid and polymer, respectively.)

In recent years, many experimental techniques have been used to measure F_c and other transport coefficients

of the colloidal particles in various polymer solutions [3–6]. While some progress has been made in understanding colloidal transport, the experimental situation, however, is complicated by the polymer adsorption, electrostatic interactions, and other effects that are peculiar to the system under study [5]. In this Letter we present measurements of F_c in a well characterized colloid-polymer system, in which the colloidal particles are approximately hard spheres and the microscopic interaction between the particle and the polymer molecule can be tuned to be either repulsive or attractive. Because the basic molecular interactions are chosen to be simple, the measurements can be used to critically examine the current theory for the colloidal transport in polymer solutions.

The colloidal particles used in the experiment consisted of a calcium carbonate (CaCO_3) core with an adsorbed monolayer of a randomly branched calcium alkylbenzene sulphonate surfactant. These particles have been well characterized previously using small-angle neutron, x-ray, and dynamic light scattering techniques [7–9]. Our recent neutron scattering measurements [10] revealed that the (CaCO_3) core radius $R_0 = 2.0$ nm and the surfactant monolayer thickness $\delta = 2.0$ nm. Thus the static (or mass) radius of the particle is 4.0 nm. The colloidal samples were prepared by diluting known amounts of the concentrated suspension with the solvent, decane. The suspension was then centrifuged at an acceleration of 10^8 cm/s² (10^5 g) for 2.5 hours to remove any aggregates and dust. The resulting suspension was found to be relatively monodispersed with $\sim 10\%$ variation in particle size, as determined by dynamic light scattering [8]. It has been shown that the particles have a hydrodynamic radius of 5.0 nm and the colloidal suspension behaves like a hard-sphere system [8,10].

The polymers used in the study were hydrogenated polyisoprene (poly-ethylene-propylene or PEP) and its single-end-functionalized derivative, which contains a

tertiary amino group capped at one end of the chain (amine-PEP). The parent PEP and its end-functionalized derivative are model polymers ($M_w/M_n < 1.1$), which have been well characterized previously using various experimental methods [11]. Decane was used as the solvent because it is a good solvent for both the colloid and the polymers [8]. Our recent scattering experiments [8,10,12,13] revealed that the pure amine-PEP solution behaves the same as the PEP solution with no association found in the amine-PEP solution. The experiments also showed that the PEP chains do not adsorb onto the colloidal surfaces, whereas the polar end groups on the amine-PEP chains interact attractively with the polar cores of the colloidal particles. It was found that the amine-PEP chains in the colloidal suspension partition themselves between the bulk solution and the adsorbed state. Because of the surfactant corona around the colloidal particles, the polymer adsorption is mitigated and typically only one chain is adsorbed on a colloidal particle [13]. Using a capillary viscometer, Davidson *et al.* [14] measured the viscosity of the polymer solution as a function of the polymer concentration C_p (g/cm^3) and found that

$$\eta_p/\eta_0 = 1 + [\eta]C_p + k_H([\eta]C_p)^2, \quad (1)$$

with $[\eta] = 2.05 \times 10^{-2} M_p^{0.73} \text{ cm}^3/\text{g}$ and $k_H = 0.35$.

In the experiment we measure the average settling velocity v_c of the particles as a function of C_p . The addition of the polymer molecules into the colloidal suspension can have two competing effects on v_c . It can either reduce v_c because the viscosity of the mixture solution is increased, or increase v_c because of the polymer-induced depletion attraction [10] between the particles. Experimentally, one can separate the two effects by changing the colloid concentration. For a sufficiently dilute colloidal suspension, the distance between the particles is so large that their interaction can be ignored. In this case, adding polymer into the suspension affects only the viscosity of the solution and v_c is simply the Stokes velocity, which is determined by the balance between the centripetal force and the viscous drag. For the sedimentation measurements to be described below, the colloid volume fraction was fixed at $\phi_c = 0.014$. At this volume fraction the colloidal interaction was found to be negligible [10]. Therefore, we have

$$v_c = \frac{2R_c^2(d_c - d_s)\mathcal{A}}{9\eta_c}, \quad (2)$$

where \mathcal{A} is the centripetal acceleration, d_s ($= 0.73 \text{ g}/\text{cm}^3$) is the solvent (decane) density, d_c ($\approx 2.0 \text{ g}/\text{cm}^3$) is the density of the particles, and R_c is their hydrodynamic radius.

Because the CaCO_3 particles are very small, their sedimentation under the earth gravity ($\mathcal{A} = g$) is unobservable. To increase the settling velocity of the particles, we used a commercial ultracentrifuge (Beckman Model L8-70M). The capacity of the sample cells was $14 \times 95 \text{ mm}$ (diameter \times height). The distance between the

middle height of the cell and the rotation axis was $\bar{r} = 11.3 \text{ cm}$. All the samples were centrifuged at the rotation rate $f = 35\,000 \text{ rpm}$ for 4 to 6 hours depending on the sample viscosity. The corresponding centripetal acceleration $\mathcal{A} = (2\pi f)^2 \bar{r} \approx 1.5 \times 10^8 \text{ cm}/\text{s}^2$ ($1.5 \times 10^5 g$), which was large enough to cause the particles to settle 1 to 5 cm toward the bottom of the cell. After the centrifugation, a sharp interface could be observed by eye in the initially uniform solution. This interface separates the upper clear solvent region from the lower dark-brown colloid-rich region. The traveling distance h of the interface was measured by a low-magnification microscope mounted on a vertical translational stage controlled by a micrometer. The experimental uncertainties for the measured h were less than 5% [15]. The settling velocity was then obtained via $v_c = h/t$, where t is the running time of the centrifugation. All the measurements were conducted at 22°C . Because the polymer density ($d_p = 0.856 \text{ g}/\text{cm}^3$) is fairly close to that of decane, sedimentation of the polymer molecules during the centrifugation is found to be negligible. To reduce systematic errors in the experiment, we present the sedimentation data in terms of the velocity ratio $v_c(C_p = 0)/v_c(C_p)$. From Eq. (2) one finds that this ratio is the normalized friction coefficient $F_c = \eta_c/\eta_0$ of the particles.

Figure 1 shows the measured F_c as a function of the polymer concentration C_p for the PEP with $M_p = 17\,500$ (in atomic mass units, same afterwards). The measured F_c first increases linearly with C_p up to $C_p \approx 0.075 \text{ g}/\text{cm}^3$ and then turns up sharply. The solid curve shows the viscosity of the polymer solution measured independently by Davidson *et al.* [see Eq. (1)]. The dashed line is the linear part of the measured viscosity $\eta_p/\eta_0 = 1 + [\eta]C_p$. Figure 1 thus reveals that the particles in the polymer solution feel the single-chain viscosity when

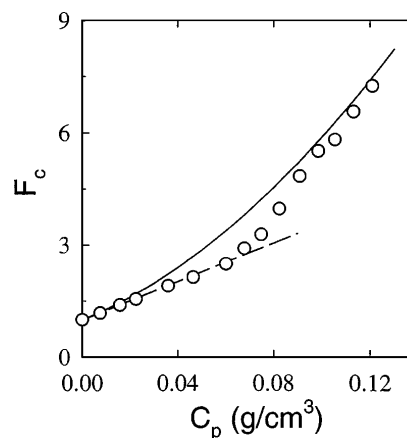


FIG. 1. Measured F_c as a function of the polymer concentration C_p for the PEP with $M_p = 17\,500$. The solid curve is the viscosity of the polymer solution measured independently by Davidson *et al.* [14]. The dashed line shows the linear viscosity.

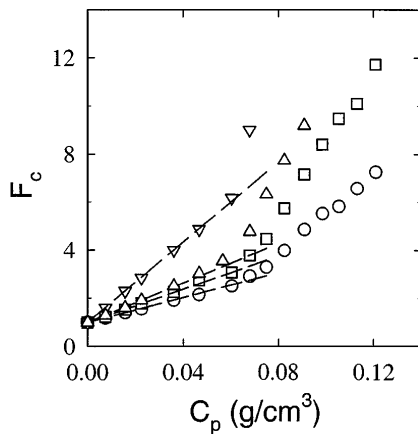


FIG. 2. Measured F_c as a function of the polymer concentration C_p for the PEP with $M_p = 1.75 \times 10^4$ (circles), 2.6×10^4 (squares), 3.3×10^4 (triangles), and 8.8×10^4 (inverted triangles). The dashed lines show the linear viscosity for the corresponding M_p .

$C_p < \tilde{C}_p$, and they experience the macroscopic viscosity of the polymer solution when $C_p \gg \tilde{C}_p$. Similar behavior of F_c was also observed for the PEP with other molecular weights. Figure 2 compares the measured F_c for the PEP with different M_p . The dashed lines show the linear viscosity $\eta_p/\eta_0 = 1 + [\eta]C_p$ for the corresponding M_p , with $[\eta]$ being given in Eq. (1). It is clearly seen that the measured F_c changes with M_p and hence does not have the scaling form $\varphi(R_c/\xi)$, as suggested by the theory [2,4].

Despite the large changes of the measured F_c with M_p , the crossover concentration \tilde{C}_p remains unchanged, as is shown in Fig. 2. We find that the transitional behavior of F_c can be well described by a switch function S_c , which is defined as

$$S_c \equiv \frac{F_c - (1 + [\eta]C_p)}{k_H([\eta]C_p)^2}, \quad (3)$$

where the values of $[\eta]$ and k_H are given in Eq. (1). Figure 3 displays the measured S_c as a function of C_p for different M_p . It is clearly shown that the transition near \tilde{C}_p ($\approx 0.075 \text{ g/cm}^3$) is a sharp and universal transition independent of M_p . Below \tilde{C}_p the particles in the polymer solution feel the single-chain viscosity (i.e., $S_c = 0$), and above \tilde{C}_p they experience the macroscopic viscosity of the polymer solution ($S_c = 1$). The measured S_c is found to be well described by a smoothed step function $S_c = \{1 + \exp[(C_0 - C_p)/\Delta C]\}^{-1}$ (the solid curve) with $C_0 = 0.077 \text{ g/cm}^3$ and $\Delta C = 0.006 \text{ g/cm}^3$. Note that the fitted ΔC , which describes the sharpness of the transition, is much smaller than the fitted crossover concentration C_0 ($\approx \tilde{C}_p$).

To understand the physical meaning of C_0 , we calculate the correlation length [2], $\xi \approx R_g(C_p/C^*)^{-3/4}$, of the polymer solution at this concentration. Here R_g is the radius of gyration of the polymer chains and $C^* =$

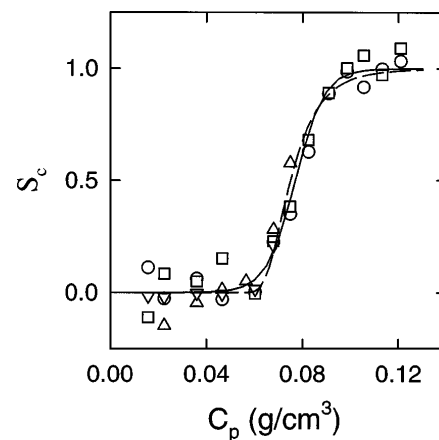


FIG. 3. Plots of S_c vs C_p for the PEP with $M_p = 1.75 \times 10^4$ (circles), 2.6×10^4 (squares), 3.3×10^4 (triangles), and 8.8×10^4 (inverted triangles). The solid curve shows the smoothed step function $S_c = \{1 + \exp[(C_0 - C_p)/\Delta C]\}^{-1}$ with $C_0 = 0.077 \text{ g/cm}^3$ and $\Delta C = 0.006 \text{ g/cm}^3$. The dashed curve is the fitted stretched exponential function $S_c = \exp[-(C_0/C_p)^\alpha]$ with $C_0 = 0.072 \text{ g/cm}^3$ and $\alpha = 9$.

$M_p/(4\pi/3)R_g^3$ is their overlap concentration. Because $R_g \sim M_p^{3/5}$, ξ is a decreasing function of C_p and is independent of M_p . Increasing C_p in the experiment, therefore, becomes equivalent to reducing the value of ξ . For the PEP with $M_p = 26000$, its $R_g = 8.3 \text{ nm}$ [10]. Thus we have $C^* = 0.018 \text{ g/cm}^3$ and $\xi \approx 3 \text{ nm}$ when $C_p = C_0$. This value of ξ is close to the particle's hydrodynamic radius R_c ($= 5.0 \text{ nm}$). As mentioned in the above, R_c is approximately 20% larger than the static (mass) radius of the particles ($R_0 + \delta = 4 \text{ nm}$). We notice that other functional forms can also be used to fit the measured S_c . The dashed curve in Fig. 3 shows the fitted function $S_c = \exp[-(C_0/C_p)^\alpha]$ with $C_0 = 0.072 \text{ g/cm}^3$ and $\alpha = 9$. This is a stretched exponential function, which has the scaling form $\varphi(R_c/\xi)$ once the concentrations (C_0 and C_p) are converted to the corresponding length scales (R_c and ξ). From Figs. 1–3 we conclude that the colloidal particles in the polymer solution feel the single-chain viscosity rather than the solvent viscosity when $R_c < \xi$, and they experience the macroscopic viscosity of the polymer solution when $R_c \gg \xi$. In the transition region, the particle's friction coefficient F_c does not have the scaling form $\varphi(R_c/\xi)$, as suggested by the theory [2,4]. Instead, the switch function S_c is found to be independent of M_p and can be described by a scaling function of R_c/ξ . The experiment suggests that the correlation length ξ in a semidilute polymer solution may not be simply viewed as a “mesh” size, below which no polymer molecules can be found. Rather, it should be considered as the size of “blobs,” inside which all the polymer monomers belong to the same polymer chain [2]. This point of view can help to explain why the colloidal particles feel the single-chain viscosity

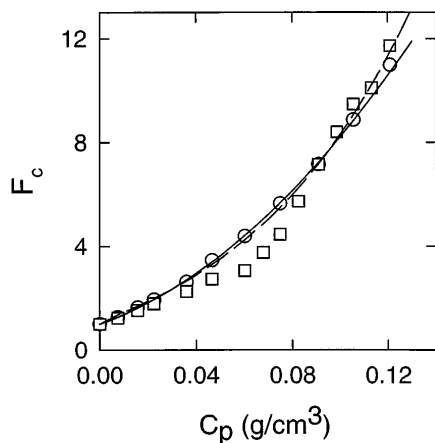


FIG. 4. Measured F_c as a function of the polymer concentration C_p for the PEP with $M_p = 26\,000$ (squares) and the amine-PEP with $M_p = 25\,000$ (circles). The solid curve shows the viscosity of the polymer solution (with $M_p = 25\,000$) and the dashed curve is the stretched exponential function $F_c = \exp[(\gamma C_p)^\nu]$ with $\nu = 3/4$ and $\gamma = 27.17 \text{ cm}^3/\text{g}$.

rather than the solvent viscosity when their hydrodynamic radius R_c becomes smaller than ξ .

We now discuss the effect of the polymer adsorption on F_c . Figure 4 compares the measured F_c for the PEP with $M_p = 26\,000$ (squares) and the amine-PEP with $M_p = 25\,000$ (circles). It is seen that the difference between the two sets of the data increases with C_p for small values of C_p up to \tilde{C}_p , and then they merge into a single curve at large values of C_p . (Because of the small difference in molecular weight, the two polymer solutions show a slightly different viscosity at the high polymer concentration end.) Figure 4 shows that the measured F_c for the amine-PEP overlaps with the viscosity of the polymer solution (the solid curve). This is because the adsorption of the amine-PEP chains on the colloidal surfaces (typically one chain per particle) makes the effective radius of the colloid-polymer aggregates always larger than the correlation length ξ . As a result, the colloidal aggregates feel the viscosity of the polymer solution at all concentrations. Note that for the colloidal samples used in the experiment, the number ratio of the particles to the polymer molecules was very small (varied from 0.25 to 0.015), and thus most amine-PEP chains were in the bulk solution. In the literature [3–6] the measured F_c is often fitted by a stretched exponential function $F_c = \exp[(\gamma C_p)^\nu]$. The dashed curve in Fig. 4 shows such a fit with $\nu = 3/4$ and $\gamma = 27.17 \text{ cm}^3/\text{g}$. We find that this function can fit only to the data with adsorption (circles) but not to those without adsorption (squares). It appears that the stretched exponential function is simply another approximate ex-

pression for the viscosity of the polymer solution. Phillies *et al.* [16] have shown that the viscosity of many polymer solutions can be well described by a stretched exponential function and our fit in Fig. 4 agrees with their finding. The fitted values of ν were found to be in between 0.55 and 1 and our value is $3/4$. Many previous investigators have argued that the measured F_c should have a scaling form, and indeed the fitted stretched exponential function can be converted to a simple exponential function $F_c = \exp[(\gamma C_p)^\nu] = \exp(R_g/\xi)$, once γ^{-1} is identified as the polymer overlap concentration C^* . In this case, however, the scaling variable is R_g/ξ instead of R_c/ξ .

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