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Self diffusion in mixtures of charged spheres

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Résumé. — On utilise la technique de diffusion Rayleigh forcée pour mesurer les constantes d'autodiffusion dans une suspension contenant deux espèces de sphères chargées qui interagissent fortement. Lorsque quelques grandes sphères diffusent au milieu d'un grand nombre de petites sphères, on trouve que leur constante d'autodiffusion est reliée simplement à la viscosité globale de la suspension par la loi de Stokes. Par contre les petites sphères se voient comme des particules discrètes et ne suivent pas la loi de Stokes. Dans le cas opposé où il n'y a que quelques petites sphères dans une suspension de grandes sphères, on trouve que les coefficients d'autodiffusion des deux espèces sont égaux. Ceci implique que la dynamique des petites sphères est alors gouvernée par le mouvement des grandes.

Abstract. — We have used the *Forced Rayleigh Scattering* technique to measure the self diffusion constant of the two separate species of charged polystyrene spheres mixed in a strongly interacting suspension. For a few large spheres diffusing in a larger density of smaller spheres, we find that the diffusion constant is simply related by Stokes law to the total viscosity of the suspension. For the same relative number of spheres the small spheres see each other as discrete particles and do not follow Stokes law with the total viscosity. In the opposite limit of a few small spheres in a sea of large spheres, we find that the self diffusion of the two species are equal. This implies that the dynamics of the small spheres are governed by the motion of the large ones.

1. Introduction.

Charged particles in suspension diffuse under the influence of Brownian motion from collisions with the solvent molecules as well as potential and hydrodynamic interactions with the other suspended particles. The self diffusion coefficient in such systems is a monotonically decreasing function of the interparticle interactions [1-4]. In systems with a small volume fraction of particles the hydrodynamic interaction can be negligible relative to the potential interactions. In turn by controlling the charge of the particle and electrolyte concentration of solvent it is possible to reduce the self diffusion by factor of order 10 from the free particle diffusion given by Stokes law ($D_0 = kT/6\pi\eta R$), before crystallization. Although there have been several studies of the self diffusion of such polyball systems, there is not a quantitative agreement between theory and experiment as one leaves the perturbation region near $D_s/D_0 \sim 1$. Nonetheless there have been phenomenological models which can predict the behaviour of monodisperse polyball systems [4].

The interaction between the charged spheres results from the screened Coulomb interaction [5]. The screening is due to the protons solvated from sulfonic acid groups on the sphere surface. Usually the polyballs are treated as discrete macroions, whereas the counterions or microions (protons) are treated as a continuous charge distribution (i.e. by using the continuum Boltzmann-Poisson equation). Recently there have been calculations which take into account the finite size of the counterion and have shown interesting and important effects in the several pair correlation functions ($S_{11}(q)$, $S_{12}(q)$, $S_{22}(q)$ where 1 refers to the macroions and 2 the microions) [6]. In order to investigate the diffusion process in more detail, test the multiple pair interaction ideas and see the relation between diffusion and viscosity we have prepared binary mixtures of polyballs of different sizes (more importantly different charges) and studied the self diffusion of each species separately. Previous work on mixtures involved the quasi-elastic light scattering from large tracer particles in a reasonably dilute suspension of small charged particles (which do not contribute

significantly to the light scattering) and found a significant decrease in the self-diffusion of the large particles [7].

2. Experimental techniques.

The technique we used was *Forced Rayleigh Scattering* [8]. The experiment consists of labelling the particles with a photochromic dye and exciting the dye with a particular pattern. The pattern is generated by splitting the beam from an ultraviolet laser and recombining it on the sample. The difference in path lengths leads to an interference pattern with sinusoidal intensity of adjustable wavelength ($2\pi/q$). The UV beam is flashed on for ~ 1 ms and leaves the particles in the high intensity region dark while in the low intensity region they remain light. The dye used in these studies was a spiropirane derivative. The dying technique and further details of the experiment are described in reference [4]. The alternate dark and light regions form a diffraction grating which is probed by a second (He-Ne) laser. The intensity of the diffracted spot is monitored by a photomultiplier tube. As the particles diffuse the diffraction grating loses contrast and the intensity of the diffracted spot decays as $e^{-2t/\tau}$, $\tau = Dq^2$. As long as the density of dyed spheres is small the coefficient D is for single labeled particles and corresponds to the self diffusion of the particles. This technique is particularly well suited for the study of mixtures since each of the species can separately be dyed and studied.

In the present study we use $0.091\ \mu$ and $0.038\ \mu$ polystyrene spheres purchased from Dow Diagnostics. The effective charge Z^* of the $0.091\ \mu$ spheres (which determine the strength of their screened Coulomb interaction using a Debye-Huckel approximation) [9] is easily determined since they crystallize at volume fractions above $\sim 0.2\%$ and their shear modulus can be measured and related to the interparticle interactions [10]. The effective charge is $Z^* \sim 300e$. The evaluation of the charge for the $0.038\ \mu$ spheres is more difficult. We have never observed the $0.038\ \mu$ spheres to crystallize, even with volume fraction up to 30% (although a glasslike state seems to exist at these highest volume fractions). The Z^* for the $0.038\ \mu$ spheres is also considerably more sensitive to the environment (concentration, solvent pH, etc.) since the ionizable surface groups are carboxylic acid which is a much weaker acid than the sulfonic acid on the $0.091\ \mu$ spheres. We have therefore performed several experiments to get an approximate value of Z^* for the $0.038\ \mu$ spheres under our experimental conditions. In the first such experiment we added either the $0.038\ \mu$ spheres or HCl to different volume fraction suspensions of the $0.091\ \mu$ spheres and determined the critical melting concentration of added electro-

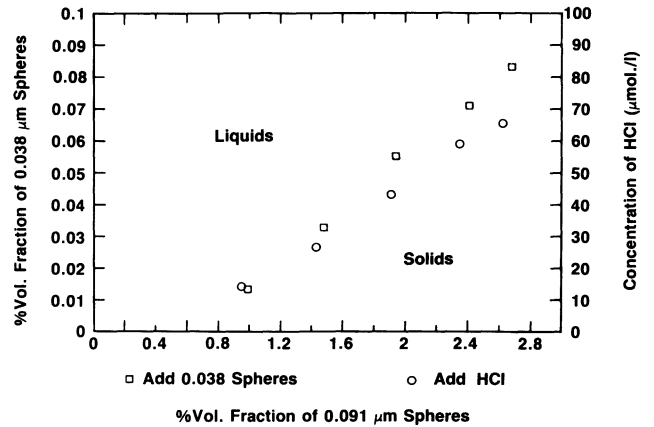


Fig. 1. — Phase boundary for melting colloidal crystals of $0.091\ \mu$ polyballs with added $0.038\ \mu$ spheres or added HCl.

lyte. The results are shown in figure 1. There is an approximate linear dependence of the melting curve with the concentration of either $0.038\ \mu$ particles or HCl indicating, but certainly not proving, that we may treat the $0.038\ \mu$ particles and their counterions as a simple electrolyte solution. We can then associate the screening length of a certain concentration of $0.038\ \mu$ particles with that of the HCl solution which melts the same colloidal crystal of $0.091\ \mu$ particles using the equation

$$\kappa^2 = \frac{4\pi e^2}{\epsilon kT} \left\{ c_{0.038} (Z_{0.038}^{*2} + Z_{0.038}^*) + c_{0.091} Z_{0.091}^* \right\} \quad (1)$$

where κ is the inverse screening length and $c_{0.038}$, $c_{0.091}$, $Z_{0.038}^*$, $Z_{0.091}^*$ are the concentrations and effective charges of the $0.038\ \mu$ and $0.091\ \mu$ particles and ϵ is the dielectric constant of water. The two terms in $Z_{0.038}^*$ arise from the screening due to the countercharges from the $0.038\ \mu$ particles (the $Z_{0.038}^*$ term) and the screening due to the $0.038\ \mu$ macroions themselves. If we allow screening from the macroions (which would be correct if the concentration of $0.038\ \mu$'s was much larger than the concentration of $0.091\ \mu$'s) then we would have $Z^* \sim 40$. If the screening is due purely to the countercharge we would find $Z^* \sim 1600$. Unfortunately, the number of $0.038\ \mu$'s is approximately equal to the number of $0.091\ \mu$'s so that neither approximation is valid. (If the value of Z^* is closer to $40e$, as we believe, then the melting is more realistically caused by the strong perturbation to the lattice of $0.091\ \mu$'s caused by the $0.038\ \mu$'s.)

We can also get an approximate value for the charge of the $0.038\ \mu$ from the viscosity of suspensions of pure $0.038\ \mu$'s using the empirical relation $\eta = G\tau$, $\tau = (0.1d)^2/D_0$, $D_0 = kT/6\pi\eta a$ [11] and the shear modulus of charged suspensions given by $G = (4/9)V(d)(Kd)^2$ where

$$V(r) = (Z^* e)^2 e^{-\kappa r} e^{2\kappa a} / \epsilon r (1 + \kappa a)^2$$

with a the sphere radius and d the interparticle spacing. Unfortunately $Z^*(G) = \text{constant}$ is a double valued function and also allows $Z^* \leq 100 e$, or $Z^* > 1000 e$ from our viscosity measurements. Finally we have measured the self diffusion of pure 0.038μ samples for low concentration and find reasonable agreement with $Z^* \sim 40-60 e$ [4]. We therefore take $Z_{0.038}^* \sim 50 e$ and in any event considerably less than $Z_{0.091}^* \sim 300 e$.

3. Large spheres labeled.

We now consider the diffusion of the large spheres in the mixtures, i.e. Forced Rayleigh Scattering experiments where the 0.091μ particles are dyed and the 0.038μ particles are not. What should we expect? First take the limit where there are a few large spheres diffusing in a much more concentrated suspension of small spheres. The large spheres undergo Brownian motion due to forces from the solvent molecules, H_2O and also from the 0.038μ spheres which in some sense comprise their own interacting fluid. In the limit that the radius of the small spheres goes to zero while their density increases to that of conventional fluids we might expect the diffusion of the large spheres to be governed by Stokes law $D_{s1} = kT/6 \pi \eta_1 r_{0.091}$ where η_1 is the viscosity of the liquid of 0.038 spheres. The large spheres are then immersed in suspension which looks like two interpenetrating fluids. In this two fluid model the diffusion constant for the large sphere is given by

$$D_s^{-1} = D_{s0}^{-1} + D_{s1}^{-1} + O(\phi) \quad (2)$$

where 0 refers to the water and 1 the fluid of interacting 0.038μ particles. The diffusion constants add reciprocally (as for rates) as long as hydrodynamic interactions (which depend on the total volume fraction of solids in suspension [$\sim 1\%$ for our studies]) are small. The viscosity in this two fluid model is simply the sum of the viscosities

$$\eta = \eta_0 + \eta_1 + O(\phi). \quad (3)$$

Similar equations have been derived with considerably more rigor by the authors of references [3] and [6] who write their equation for the self diffusion as $D_s = kT/(\zeta_0 + \Delta\zeta)$ where ζ_0 is the friction factor related to the suspending fluid and $\Delta\zeta$ is the friction factor related to the interparticle potential interactions. Clearly this equation can be written in the form of equation (2). In suspensions with a single species, equations (2) and (3) have been found to describe and predict experimental results excellently [4, 12].

We can obtain complementary information on these suspensions by measurements of their viscosity. In the present study this was accomplished by observing the *fall time* of a small ion exchange resin

bead in the sample couvette directly after each measurement of the self diffusion and comparing the fall time with that of the same bead in the same couvette filled with water. The viscosity measured in this way corresponded well to the macroscopic zero shear rate viscosity measured in a Zimm viscometer for a similar sample. The accuracy of the *fall time* measurements is $\sim 5\%$.

The normalized large sphere diffusion (D_s/D_0) and normalized viscosity from our measurements are plotted in figure 2. The x axis of this plot is the volume fraction of 0.038μ spheres with the total volume fraction of spheres being kept constant at 1% . Thus $x = 0$ corresponds to a pure 1% suspension of 0.091μ particles while $x = 1$ corresponds to a pure 1% suspension of 0.038μ particles.

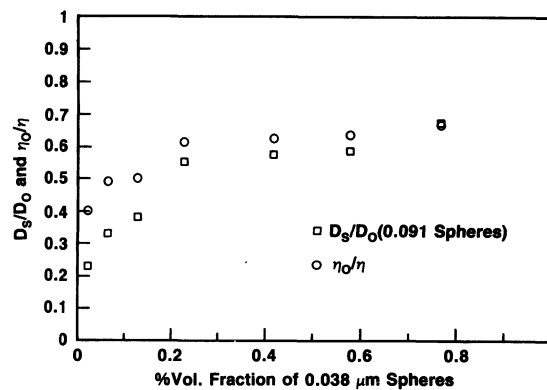


Fig. 2. — Self diffusion constant for 0.091μ spheres (normalized by their free diffusion constant) for mixtures of 0.091μ and 0.038μ spheres with constant 1% total volume fraction. On the abscissa is the volume fraction of 0.038μ spheres, 0 corresponds to 1% pure 0.091 's, 1% to pure 0.038 's. Also shown is the reciprocal normalized viscosity measured for each sample.

Near $x = 1\%$ there are a few large particles surrounded by the small particles, the case we began considering above in writing equations (2) and (3). From these equations we may try to obtain the normalized self diffusion by assuming Stokes diffusion in the two separate interpenetrating fluids, $D_{s0} = D_0 = kT/6 \pi \eta_0 r_{0.091}$ and

$$D_{s1} = kT/6 \pi \eta_1 r_{0.091}.$$

This yields the simple result $D_s/D_0 = \eta_0/\eta$. In the region near $x = 1\%$ of figure 2, we see that D_s/D_0 for the large particle fits nicely with the measured reciprocal viscosity. Thus the large spheres are apparently undergoing free diffusion in a complex fluid of viscosity η . However, as the large particles begin to interact with each other this relation breaks down.

Suppose we are at the other side of figure 2 near $x = 0$ where the large spheres interact primarily with

other large spheres. In this case the particles see each other as individual particles rather than as a quasicontinuous liquid. Presumably we should be able to calculate the diffusion of the particles from knowledge of their interactions but as discussed toward the beginning of this paper, theories have not yet been able to successfully treat this strongly interacting case. The problem however is similar to a species diffusing in a liquid consisting of the same species, i.e. an atom of argon diffusing in liquid argon. Although there is little theoretical justification, phenomenologically it is well known for all simple liquids that the molecular self diffusion is given by $(kT/3.3 \pi \eta R)$ where R is the particle radius, a result which resembles Stokes law but for the substitution of 3.3π for 6π [13]. To apply such a formula to our case it is more appropriate to use $1/2$ the interparticle separation for R (instead of the polyball radius) since it is the interparticle forces that are important not the particle sizes, when considering the polyballs as a separate fluid. For the nearly pure, 1 %, 0.091μ suspension $1/2$ the interparticle spacing is 0.19μ and the measured viscosity $\eta/\eta_0 = 2.6$ yields a value of $D_{s1} = 9.2 \times 10^{-9}$, $D_0 = 4.8 \times 10^{-8} \text{ cm}^2/\text{s}$ and the self diffusion D_s is then calculated as $0.22 D_0$ which agrees very well with the experimental observation in figure 2 and is significantly different from η_0/η .

4. Small spheres labeled.

We now look at the self diffusion of the 0.038μ spheres in another similar set of mixtures with only the small spheres dyed, figure 3. For $x \sim 1$ we have small spheres diffusing in a liquid of small spheres. Using the same arguments as above D_{s1} should correspond to molecular motion in a simple liquid. With 1 %, 0.038μ suspension, $1/2$ the interparticle

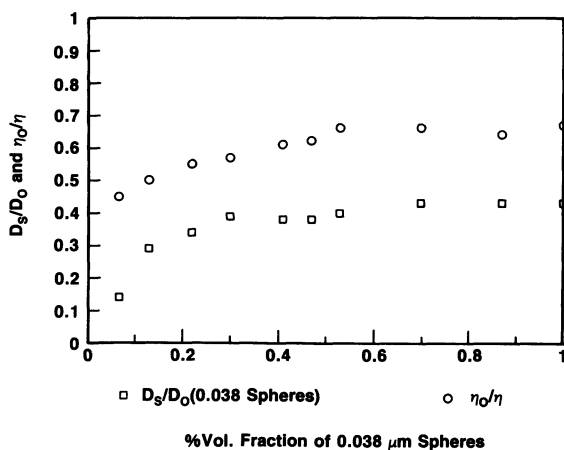


Fig. 3. — Normalized self diffusion constant for 0.038μ spheres in 1 % mixtures with 0.091μ spheres. The reciprocal normalized viscosity for these samples is also shown.

spacing is 0.079μ , the viscosity $\eta/\eta_0 = 1.5$, $D_{s1} = 1.01 \times 10^{-7}$, $D_0 = 1.15 \times 10^{-7} \text{ cm}^2/\text{s}$ and $D_s/D_0 = 0.47$, in agreement with measurement and very different from η_0/η .

The most interesting situation occurs when we have a few labelled small spheres diffusing in a sea of interacting large spheres. In this case the small particles see the particles of the liquid they are in individually, but they are a different species. The probe particle has smaller size and more importantly smaller potential interactions. In one limit, for small charge (for example that of a simple counterion) we might expect a fast diffusion approaching free diffusion. Of course as the charge is increased to that of the large spheres the diffusion will be slowed to that of the large spheres. In figure 3 we see that there is a strong reduction in D_s in the region near $x = 0$. What is more illuminating is the data replotted in figure 4 without normalization by D_0 for each species. What we see in this figure is that the absolute value of the diffusion constant of the small spheres approaches that of the large spheres in the $x \sim 0$ regime. Actually there were separate samples used to make the measurements for large and small spheres and their viscosities were slightly different. If we try an analysis such as above with $D_s = kT/3.3 \pi \Delta \eta R$ we find $R = 0.16 \mu$ for 0.091 in 0.091 and $R = 0.18 \mu$ for 0.038 in 0.091 , which still suggests that the diffusion constant of the small spheres is approaching that of the large spheres.

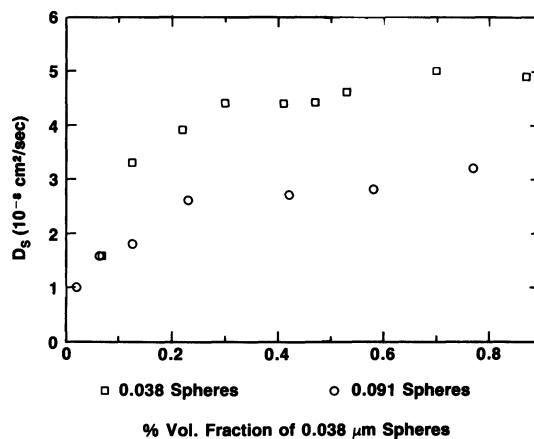


Fig. 4. — Absolute values of the diffusion constants for the two species in 1 % mixtures of 0.091μ and 0.038μ polyballs as a function of the volume fraction of 0.038μ 's. Note the similarity in D_s in the regime where the dominant species is the large spheres.

5. Discussion.

A simple explanation of this unusual result would be that the small spheres are trapped in cages by the large spheres and that the only way they can move is

for the cages to open by diffusion of the large spheres. Thus the diffusion of the small trapped spheres would be controlled by that of the large spheres. While this may be qualitatively correct it would be somewhat surprising if the cages would have to open as far to let a small sphere pass as to let a large sphere pass. In any event these results largely suggest that the self diffusion of a particle is governed mostly by some large scale motion of many other particles rather than the particular properties of the local potentials in which it resides.

In conclusion we have studied the self diffusion of strongly interacting charged particles in binary mixture suspensions. For a few large particles diffusing

in a sea of small particles the diffusion obeys Stokes law with the use of the macroscopic viscosity. For particles diffusing amongst like particles the phenomenology associated with simple fluids works well. The interesting case of a few small spheres diffusing in many large spheres yields the unexpected result that the two spheres have almost the same diffusion rate indicating that diffusion in these strongly interacting fluids is controlled by cooperative motion of large groups of particles.

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