Theor Chim Acta (1992) 82: 419–423

Theoretica Chimica Acta

Short-time mobility of spherical particles in concentrated aqueous dispersions determined by diffusing wave spectroscopy

Leeyih Wang and Wilmer G. Miller

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

Received April 11, 1991; received in revised form May 17, 1991/Accepted June 10, 1991

Summary. The diffusion of optically dense, charge stabilized, polystyrene latex spheres of 500 nm radius in water at 25°C was determined by diffusing wave spectroscopy in the backscattering mode. The diffusion coefficient of the latex spheres had a value of $4.8 \times 10^{-13}\,\mathrm{m^2\,s^{-1}}$ at infinite dilution and monotonically decreased as the number density of latex spheres increased. The diffusion coefficient dropped by a factor of 3 at 38 volume % latex and a factor of 20 at 59 volume % latex. Comparison was made to diffusion of sterically stabilized poly(methyl methacrylate) latex in refractive index matched mixed organic fluids as determined by dynamic light scattering. The concentration dependence determined by diffusing wave spectroscopy matched closely to the short-time diffusion determined by dynamic scattering and not to the long-time diffusion. Although the difference in repulsive potential between the charge and the sterically stabilized lattices must be large, it has a surprisingly small effect on the translational diffusion of the latex over distances small compared to the intersphere distance.

Key words: Spherical particles – Diffusion wave spectroscopy – Short-time diffusion

1. Introduction

The motion of spherical particles as a function of their number density is of theoretical as well as practical interest. Particles may range from atomic to colloidal dimensions. Spherical polymer latex particles may be produced which are very uniform in size with diameters ranging from hundreds to thousands of nanometers. They must be dispersed in a fluid, preferably one that does not swell the latex particles, in order to have motion. Short-time motion, displacements small compared to intersphere distance, as well as long-time motion is of importance. At very low particle concentration diffusion is Brownian with little interparticle interaction. At higher particle concentrations both collective and self-diffusive modes become significant. Eventually a number density is reached where particle diffusion is restricted by an effective cage composed of surrounding particles with only occasional escape. At some number density a phase transition to an ordered phase may occur.

Dynamic light scattering (DLS), photon correlation spectroscopy, has long been used to determine translational diffusion in dilute latex systems. Typically latex spheres are dispersed in an aqueous media and stabilized by the presence of ionic groups on the latex surface. The difference between the refractive index of the organic latex particle and water, together with the latex size, limits conventional DLS studies to low latex concentrations due to the rapid rise of multiple scattering as the concentration is increased. Multiple scattering may become so severe that a few percent dispersion may already be milky white; however, diffusion in dispersions ten times as concentrated is of interest. One approach to circumvent multiple scattering is a switch to a mixed solvent system which nearly matches the refractive index of the latex spheres. Short-time diffusion of poly(methyl methacrylate), PMMA, latex spheres in mixed solvents composed of carbon disulfide with decalin, hexane or dodecane has been determined to a volume fraction of 0.5 [1–4]. In order to stabilize the latex particles against aggregation in these fluids the latex must be sterically stabilized, i.e., coated with a monolayer of polymer having tails and loops extending into the suspending fluid, thus introducing a small uncertainty in particle diameter. By the introduction of a second set of spheres of equal diameter but different refractive index long-time diffusion has been studied also [3, 4].

Recently [5–8] a scattering technique, termed diffusing wave spectroscopy (DWS), has been introduced which allows the determination of short-time diffusion in multiply scattering systems. In fact it can only be used in systems with intense multiple scattering, and the theoretical interpretation of the data rests on the diffusive nature of the transport of light in the very strongly multiply scattering regime. In this communication the concentration dependence of the diffusion of charge stabilized polystyrene latex in water is determined by DWS in the backscattering mode, and compared with diffusion of sterically stabilized latex in organic solvents determined by DLS.

2. Experimental

Polystyrene (PS) latex spheres were prepared in an emulsifier free system composed of 10% inhibitor scrubbed sytrene monomer in water stirred by a rotating paddle at 385 rpm under nitrogen at 70°C. Polymerization was initiated with potassium persulfate (1 mM) and allowed to proceed for 27 h. The resulting latex spheres are charge stabilized by covalently attached sulfate groups as a consequence of chain initiation by sulfate radical ions. The latex preparation was spin coated onto glass and the particles were viewed by scanning electron microscopy. It was also diluted and the PS sphere diffusion coefficient determined by DLS.

DLS was performed using a 2 W argon laser at 5145 Å and cylindrical sample cells in a spectrometer previously described [9]. The scattering intensities were received at 90 degrees by a Pacific 126 photometer and analyzed by a Langley–Ford Model 1096 correlator. The homodyne correlation function was analyzed by the cumulant method.

For DWS measurements the DLS spectrometer was modified with an optical setup similar to Weitz et al. [10], where the condensing lens is removed prior to the light beam entering the sample cell, a 10 mm × 75 mm flat cell with a 1.0 mm path length. The scattered light that was collected was polarized perpendicular to and 160 degrees from the incident beam, coming through a 50 μm diameter pinhole. The backscattered light was collected from a large area of the sample. The raw data from the correlator were normalized by first subtracting the baseline, the average of the last 16 channels in the correlator, followed by dividing all channels by the value in the first channel. The latex concentration was adjusted by solvent evaporation, and introduced into the sample cell through a syringe. The sample was placed in a thermostated (25°C) cell holder mounted on a vibration isolation table and allowed to equilibrate in the spectrometer for one hour before data were collected.

3. Results and discussion

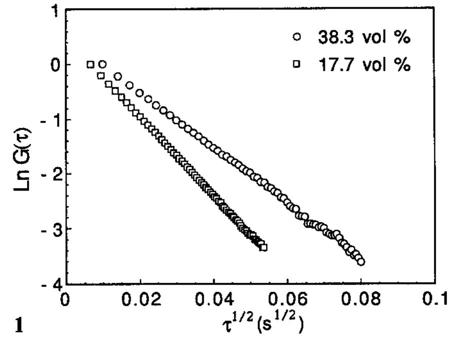
The polystyrene latex was determined by scanning electron microscopy to have a radius of 500 ± 20 nm. The latex preparation was then diluted ten-thousand fold and the latex diffusion coefficient determined by DLS. The diffusion coefficient, $4.82 \pm 0.27 \times 10^{-13}\,\mathrm{m^2\,s^{-1}}$, corresponds to a sphere radius of 510 ± 28 nm as determined from the Stokes–Einstein equation. The radius determined by electron microscopy, a number average value, is in good agreement with the DLS radius, a z-average value. The latex is quite uniform in particle size.

Theory underlying DWS predicts [6] the intensity correlation function, $G(\tau)$, should decay exponentially as the square root of time τ, as given by:

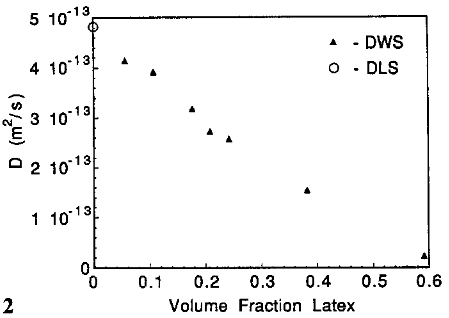
$$G(\tau) = \exp[-2\gamma(6\tau/Dk_0^2)^{1/2}] \quad (1)$$

where k_0 is the wave vector, $2\pi/\lambda$, D is the translational diffusion coefficient and γ is a multiplicative factor modifying the diffusion length and is expected to be independent of concentration [11]. Typical plots of the experimental data are shown in Fig. 1. The decay follows Eq. (1) well; however, diffusion coefficients cannot be determined without a knowledge of γ. Inasmuch as D was only known at infinite dilution from DLS measurements, slopes from plots as in Fig. 1 were extrapolated to infinite dilution and γ calculated. This value, 1.6, was then used in determining D using Eq. (1). The results are shown in Fig. 2. The highest concentration is greater than that where crystallization is normally expected to occur [12]. We have no knowledge concerning crystallization in this sample.

The diffusion of latex spheres may depend on several factors – size of the spheres, concentration, and the nature of the repulsive interactions which stabilize them, especially electrostatic versus steric stabilization. Shown in Fig. 3 is a comparison between the diffusion of the 500 nm, charge stabilized, aqueous media PS latex determined by DWS and 83 nm, sterically stabilized, organic media PMMA latex determined by DLS [3]. Several points with respect to the DLS data need to be mentioned. The short-time values were determined in a CS_2/hydrocarbon indexed matched media whereas the long-time values are for PMMA spheres dispersed in a poly(vinyl acetate) latex index matched with a *cis*/*trans*-decalin media. The PMMA latex diffusion is plotted against the total latex concentration. Furthermore, the latex concentrations were calculated making an assumption concerning the contribution of the steric stabilizer to the effective latex size. The virtual coincidence of the short-time DLS data with the DWS data suggests that the concentration dependence of the normalized (D/D_0) diffusion is independent of sphere size as expected, that there is little difference in diffusion at high number densities between the charge stabilized and the sterically stabilized latex, and that the DLS measurement gives short-time



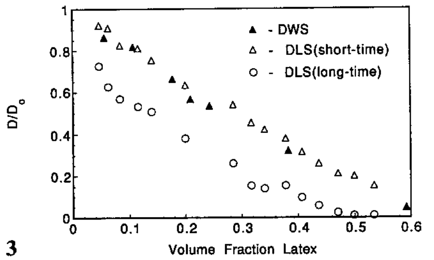
1



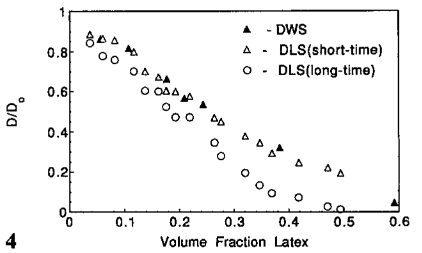
2

Fig. 1. Decay of the intensity correlation function by DWS in the backscattering mode for two concentrations of 500 nm polystyrene latex at 25°C

Fig. 2. Translational diffusion coefficients of polystyrene latex spheres as a function of concentration in aqueous media



3



4

Fig. 3. Comparison of PS latex diffusion (DWS) in water with short- and long-time diffusion (DLS) of sterically stabilized PMMA in mixed organic solvents [3]

Fig. 4. Comparison similar to Fig. 3 except the PMMA latex spheres were 205 nm and the long-time diffusion was of silica particles in the PMMA/CS_2/decalin media. Again the latex concentration includes the estimated volume of the steric stabilizer [4]

diffusion, as had been theoretically predicted [10, 13, 14]. This is further reinforced in Fig. 4, where comparison is made of the DWS measured diffusion with short-time diffusion of 216 nm radius sterically stabilized PMMA latex in CS_2/decalin and of long-time diffusion of 205 nm sterically stabilized silica particles in the PMMA latex/CS_2/decalin media [4]. Again the latex concentration includes the volume contribution of the steric stabilizer, estimated in this case to be 1.154 times the volume of the bare latex particles [4].

The observation that the concentration dependence of D/D_0 is not a function of sphere size is well known from dynamic light scattering [3, 4], though models using multibody hydrodynamic interactions do not always fit the measured dependence [1]. Although we believe this study to be the first comparison between DWS in the backscattering mode and DLS over a wide concentration range, it is not surprising that the DWS data should compare to the short-time DLS data [10, 14]. What is surprising, however, is that the short-time diffusion of this charge stabilized latex in water appears to match well that of the nonionic, sterically stabilized latex dispersed in nonpolar media. Dilute dispersions of charged particles in water exhibit long range Coulombic repulsions. There is reasonable agreement between theory and experiment [15–18]. In the simplest approximation the Coulombic repulsion gives an effective hard-core sphere diameter larger than the true particle diameter, particularly in the system studied here where there is no supporting electrolyte to shrink the double layer thickness. The sterically stabilized spheres are expected to have a hard-core size that is little different from that of the bare latex. Although the conformation of the steric stabilizer, poly(12-hydroxystearic acid), on the latex sphere is unknown, the comparisons in Figs. 3 and 4 will be altered only slightly if adjustments are made for the contribution of the steric stabilizer. In fact, if one completely neglects the volume contribution to the sterically stabilized latex, D/D_0 follows off more rapidly with concentration in the sterically stabilized latex than in the charge stabilized one. It may be necessary to systematically vary the latex charge in order to understand this result. Since the experimental results reported here were completed, two reports have appeared on the diffusion of charge stabilized latex using DWS in the transmission rather than the backscattering mode [19, 20]. These also report diffusion coincident with short-time diffusion of sterically stabilized latex spheres. However as electrolyte was added in both cases to suppress the double layer, coincidence with sterically stabilized spheres is not as surprising as in our results.

Acknowledgments. We wish to acknowledge support from the NSF-Center for Interfacial Engineering, from the Graduate School, University of Minnesota, and from the Research Corporation.

References

1. Pusey PN, vanMegen W (1983) J Phys (Paris) 44:285
2. vanMegen W, Ottewill RH, Owens SM, Pusey PN (1985) J Chem Phys 82:508
3. Ottewill RH, Williams N St J (1987) Nature 325:232
4. vanMegen W, Underwood SM (1990) Langmuir 6:35
5. Maret G, Wolf PE (1987) Z Phys B65:409
6. Pine DJ, Weitz DA, Chaikin PM, Herbolzheimer E (1988) Phys Rev Lett 60:1134
7. Maret G, Wolf PE (1989) Physica Scripta T29:223
8. MacKintosh FC, John S (1989) Physical Review B 40:2383
9. Russo PS (1981) PhD Thesis, University of Minnesota
10. Pine DJ, Weitz DA, Maret G, Wolf PE, Herbolzheimer E, Chaikin PM (1990) In: Shen P (ed) Scattering and localization of classical waves in random media. World Scientific Publ, Singapore, p 312
11. Horne DS (1989) J Phys D 22:1257
12. Alder BJ, Hoover WG, Young DA (1968) J Chem Phys 49:3688
13. Pine DJ, Weitz DA, Chaikin PM, Herbolzheimer E (1990) In: OSA Proc on Photon Correlation Techniques and Applications, vol 1, Optical Society of America, Washington, p 35
14. Pine DJ, Weitz DA, Pusey PN, Tough RJA (1989) Phys Rev Lett 63:1747
15. Hess W, Klein R (1980) J Phys A 13:65
16. Gaylor K, Snook I, vanMegen W (1981) J Chem Phys 75:1982
17. Ohtsuki T (1981) Physica A 108:441
18. Ohtsuki T (1982) Physica A 110:606
19. Fraden S, Maret G (1990) Phys Rev Lett 65;512
20. Qiu X, Wu X, Xue J, Pine D, Weitz D, Chaikin P (1990) Phys Rev Lett 65:516