Structural and dynamic properties of colloidal liquids and gases of silica spheres (29 nm in diameter) as studied by the light scattering measurements

Abstract Static and dynamic light-scattering measurements are made for colloidal-liquids and -gases of silica spheres (29 nm in diameter) in the exhaustively deionized aqueous suspension and in the presence of sodium chloride. Single broad peak is observed in the light-scattering curve and the liquid-like and gas-like distributions have been observed. Colloidal crystals are not formed at any sphere concentrations. The nearest-neighbor interparticle distances of colloidal liquids, \( l_{\text{obs}} \), agree excellently with the effective diameters of spheres \( (d_{\text{eff}}) \) including the electrical double layers in the effective soft-sphere model and also with the mean intersphere distances, \( l_o \), calculated from the sphere concentration, i.e., \( l_{\text{obs}} \approx d_{\text{eff}} \approx l_o \). This relation supports the importance of the electrostatic interparticle repulsive interaction. Two dynamic processes have been extracted separately from the time profiles of autocorrelation function of colloidal liquids. Decay curves of colloidal gases are characterized by the single translational diffusion coefficients, which are always lower than the calculation from the Stokes-Einstein equation using true diameter of spheres and increase as ionic concentration increases. These experimental results emphasize the importance of the expanded electrical double layers and the electrostatic intersphere repulsion on the structural and dynamic properties of the colloidal liquids and gases.

Keywords Light scattering · Colloidal liquids · Colloidal gases · Colloidal silica spheres

Introduction

Colloidal suspensions display the extraordinary structures in particle distribution, such as crystal-like distributions especially in the deionized state \([1, 2, 3, 4, 5, 6]\). This structural peculiarity has been explained mainly with the extended electrical double layers formed around the particles and the electrostatic interparticle repulsion \([1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]\).

Ionic groups either dissociated or adsorbed on the colloidal surfaces leave their counterions in suspension, and these excess charges accumulate near the surface forming an electrical double layer. The counterions in the diffuse region in the double layer are distributed according to a balance between the thermal diffusive forces and the forces of electrical attraction with colloidal particles. The thickness of the double layers is approximated with the Debye-screening length \( (l_{DH}) \):

\[
l_{DH} = \left( \frac{4\pi^2 n/k_B T}{e^2} \right)^{-1/2},
\]

where \( e \) is the electronic charge, \( \epsilon \) is the dielectric constant of the solvent, \( k_B \) is the Boltzmann constant, and \( n \) is the concentration of free-state cations and anions in suspension, and is given by \( n = n_c + n_+ + n_- \), where \( n_c \) is the concentration (number of ions per cm\(^3\)) of diffusible...
counterions, $n_i$ is the concentration of foreign salt, sodium chloride in this work, and $n_a$ is the concentration of both H$^+$ and OH$^-$ ions from the dissociation of water. In order to estimate $n_a$, the fraction of free counterions ($\beta$) must be known, since most counterions are bound tightly with the ions of the colloidal surface [7, 17, 18, 19, 20]. Note that $\beta$ of silica spheres is estimated to be 0.1 [19, 20] and the largest value of $l_{DH}$ is ca. 1 µm in water.

According to the effective soft-sphere model [21, 22, 23, 24, 25, 26, 27], which is a simple but very convenient assumption especially for the deionized colloidal suspension, crystal-like ordering is formed when the effective diameter ($d_{eff}$) of the spheres including the Debye-screening length is close to or larger than the intersphere distance ($l$), i.e., $d_{eff} = [diamet\, (d_a) + 2 \times l_{DH}] > l$. In crystal-like structures, the spheres fluctuate around their equilibrium positions. When $d_{eff}$ is comparable to or shorter slightly than the $l$ value, the distribution of the spheres is usually liquid-like and the spheres move with translational diffusion, though the effective concentration is higher than the stoichiometric concentration due to the extended electrical double layers. When $d_{eff}$ is much shorter than $l$, a gas-like distribution is observed. Note that the observed intersphere spacing ($l_{obs}$) is always close to the calculated mean intersphere distance ($l_o$) and $l_o$ can be safely replaced with $l$.

It should be noted here that the electrical double layers may not be formed firmly when the sphere size is not large enough compared with the simple ions, since the small spheres move very vigorously by Brownian motion. It is highly plausible that the critical concentration of crystallization of colloidal spheres depends mainly on the mean sphere size and the monodispersity of the spheres, though other factors such as suspension temperature, viscosity and dielectric constant of solvent, and charge density of spheres are also important. When highly polydispersed spheres are used, the sphere distribution comes to be amorphous-solid instead of crystal-like [28]. From our experiences, the spheres smaller than 50 nm in diameter did not form crystal-like structure in the exhaustively deionized and diluted suspensions [29, 30]. However, this critical size will decrease further in future when the monodispersity of the spheres is improved greatly. One of the main purposes of this work is to check whether the colloidal spheres of 29 nm in diameter form crystal-like distribution or not in deionized suspension.

Difference in distribution between the crystal-like and liquid-like is clear when the structure factor, $S(q)$ term is derived from the scattering curves and the theory on the particle form factor, $P(q)$. For colloidal crystals very sharp peaks, which are well assigned to the respective lattice planes, appear. On the other hand, $S(q)$ term of the colloidal liquids shows the single broad peak or multiple sharp peaks (their intensities decrease rapidly from the primary to secondary, tertiary, continuously) for disordered and ordered liquids, respectively [31]. It is interesting to note here that the dynamic modes of fluctuation of spheres at the liquid-crystal transition region do not differ between them so much [31]. In particular, the synchronous mode of the translational movement of spheres plays an important role for the structure formation of liquid and crystal structures similarly. Another interest of this work is to clarify the structural and dynamic nature of the liquid-like structure of small colloidal spheres.

Static (SLS) and dynamic light scattering (DLS) techniques are known as ones of the most precise methods for determining sphere diameter and are also suitable for study of dynamics of interacting particle systems [32, 33, 34, 35, 36, 37, 38, 39, 40, 41]. However, several researchers including us have experienced that the diameter of colloidal spheres estimated by the DLS method is often a bit larger (within 10% in most cases) than that obtained from electron microscopy. This difference has often been beyond the extent explainable by the shrinking of spheres in the course of drying for the latter technique, and should be related to the significant role of the electrical double layers formed around the colloidal particles.

Several years ago we reported the extraordinary translational-diffusion behavior of colloidal spheres in deionized suspension by using a metallurgical microscope [42]. The translational self-diffusion coefficients of polystyrene spheres, 120 nm in diameter, decreased sharply as NaCl concentration decreased. We also found that the rotational diffusion coefficients of ellipsoidal colloids of tungstic acid [43, 44] and poly(tetrafluoroethylene) [45] colloids decreased as the ionic concentration of suspension decreased. These observations have been interpreted in terms of the extended electrical double layers. This work also aims to clarify the role of the electrical double layers on the translational diffusion of colloidal particles in the gas-like state.

**Experimental**

Materials. Colloidal silica spheres of CS22P was a gift from Catalyst & Chemicals Ind. Co. (Tokyo). Diameter ($d_s$), standard deviation ($s$) from the mean diameter, and polydispersity index ($s/d_s$) were 29 nm, 6 nm, and 0.21, respectively. $d_s$ and $s$ were determined from an electron microscope. The charge density of the spheres was determined by conductometric titration with a Wayne-Kerr autobalance precision bridge, model B331, mark II (Bognor Regis, Sussex). Charge density of strongly acidic groups was 0.48 µC/cm$^2$. The sphere sample was carefully purified several times using an ultrafiltration cell (model 202, membrane: Diaflo-XM300, Amicon Co.). Then the sample was treated on a mixed bed of cation- and anion-exchange resins [Bio-Rad, AG501-X8 (D), 20–50 mesh] more than one year before use, since the newly produced silica spheres release a considerable amount of alkali ions from sphere surfaces for a long time. Water used for the purification and for suspension preparation was purified by a Milli-Q system (Milli-RO5 plus and Milli-Q plus, Millipore Co., Bedford, MA).