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Structure and Dynamics of Bimodal Colloidal Dispersions in a Low-Molecular Weight Polymer Solution

Fan Zhang^{1,*}, Andrew J. Allen¹, Lyle E. Levine¹, De-Hao Tsai², and Jan Ilavsky³

¹Material Measurement Laboratory, National Institute of Standards and Technology Gaithersburg, MD 20899, USA

²Department of Chemical Engineering, National Tsing Hua University Hsinchu, Taiwan, Republic of China

³X-ray Science Division, Advanced Photon Source, Argonne National Laboratory Argonne, IL 60439, USA

Abstract

We present an experimental study of the structural and dynamical properties of bimodal, micrometer-sized colloidal dispersions (size ratio ≈ 2) in an aqueous solution of low-molecular weight polymer (polyethylene glycol 2000) using synchrotron ultra-small angle X-ray scattering (USAXS) and USAXS-based X-ray photon correlation spectroscopy. We fixed the volume fraction of the large particles at 5 % and systematically increased the volume fraction of the small particles from 0 % to 5 % to evaluate its effect on the structure and dynamics. The bimodal dispersions were homogenous through the investigated parameter space. We found that the partial structure factors can be satisfactorily retrieved for the bimodal colloidal dispersions using a Percus-Yevick hard sphere potential when the size distributions of the particles were taken into account. We also found that the partial structure factor between the large particles does not exhibit significant variation with increasing volume fraction of small particles, whereas the isothermal compressibility of the binary mixture was found to decrease with increasing volume fraction of small particles. The dynamics of single-component large particle dispersion obey the principles of de Gennes narrowing, where the wave vector dependence of the interparticle diffusion coefficient is inversely proportional to the interparticle structure factor. The dynamics of the bimodal dispersions demonstrate strong dependence on the fraction of small particles. We also made a comparison between the experimental effective dynamic viscosity of the bimodal dispersion with theoretical predictions, which suggest that the complex mutual interactions between large and small particles have a strong effect on the dynamic behaviors of bimodal dispersions.

Graphical abstract

*correspondence fan.zhang@nist.gov.

Introduction

Colloidal dispersions, which consist of nanometer-to-micrometer sized particles in a suspending medium, are ubiquitous both in nature and in everyday life.¹ They offer a wide variety and the tunability of their interparticle interactions that explain their importance in industrial applications and basic research. Fundamentally, as surrogate systems, colloidal dispersions have been extensively used to characterize the thermodynamic behaviors of atomic liquids because of the similarities between their equilibrium structures.² They have also been proven as pivotal model systems for understanding critical equilibrium phase transitions such as crystallization^{3–4} and melting transitions^{5–6}. Meanwhile, the pairwise interaction potentials between colloids are highly tunable due to the existence of many different forms of possible interactions. The balance of forces that act upon the ensemble of particles affects the dispersion stability, which in turn decides the overall bulk properties of colloidal dispersions that greatly impact their applications in the pharmaceutical, chemical, oil, and ceramics industries. From a physical point of view, such effects often manifest themselves in the form of their static structures and equilibrium dynamics. Therefore, understanding the structural and dynamical behaviors of colloidal dispersions is a necessary step in the better design and tailoring of colloidal products.

Colloidal dispersions are inevitably complex due to the high degree of statistical freedom inherent to many-body systems. In order to reduce the level of complexity, many existing studies have focused extensively on dispersions of monodisperse or pseudo-monodisperse spherical particles, the simplest form of colloidal dispersions.⁷ Research on these ideal model systems has unveiled many physical, chemical, and engineering aspects of colloidal dispersions, ranging from their thermodynamics⁸, transport properties⁹, response to external field and stress^{10–11}, and rheological behaviors^{12–13}, and to a large extent, established the foundation of colloidal science as we know it today.

Naturally occurring and industrially used colloidal dispersions are overwhelmingly polydisperse in size. The scientific and technological relevance of polydispersity is clear. To assess the effects of polydispersity, a natural extension, and perhaps the most obvious approach, is to evaluate the materials properties of bimodal colloidal dispersions. Bimodal dispersions demonstrate much richer physical phenomena not only due to their differences in

size, but also due to a greater variety of interparticle interactions between particles of different species. Experimentally, the structures and phase behaviors^{14–20}, liquid order^{21–22}, equilibrium dynamics,²³ crystal formation^{24–26}, gelation²⁷, shearing²⁸, and segregation²⁹ of a number of bimodal dispersion systems, including mixtures of hard spheres, charged spheres, charged and uncharged spheres, charged and sterically stabilized spheres, have been studied under many different dispersion conditions. Theoretical modeling and computer simulations have also made great strides in predicting the phase diagrams^{30–33}, gelation transitions³⁴, viscosity,^{35–37} and diffusive properties^{38–39} of bimodal dispersions, much of which are still to be observed experimentally.

Another common approach to increase the level of complexity in the colloidal dispersions is to introduce non-adsorbing polymers to a monodisperse colloidal dispersion⁴⁰. The addition of non-adsorbing polymers to a colloidal dispersion can induce an attractive depletion-type interparticle interaction whose depth and range can be readily tuned by altering the concentration and molecular weight of the polymers. Equilibrium phase behavior⁴¹, diffusion dynamics,^{23, 42–46} and the metastable gel or glass states⁴⁷ induced by polymer bridging or depletion have been investigated on model systems. These findings, in turn, form important reference points for understanding more complex colloidal dispersions.

In spite of the extensive experimental, analytical and simulation efforts devoted to the studies of colloidal dispersions, substantial gaps still remain in the vast parameter space characteristic of these systems. A class of systems of particular importance that has rarely been investigated is polydisperse colloidal dispersions suspended in a medium that contains low molecular weight polymers in water. Examples include human blood, where plasma contain a variety of low-molecular-weight proteins⁴⁸, as well as water streams, where the nominal molecular weights of humic and fulvic acids have been found to be between 1000 and 2000.⁴⁹ An understanding of their behaviors, therefore, has much bearing to both biological and environmental science and engineering.

In this study, we make use of synchrotron-based small angle X-ray scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS) to probe the polydispersity effects on the structure and dynamics of model bimodal colloidal dispersions in an aqueous solution of sufficiently concentrated low-molecular weight polymer solutions, in the hope of obtaining an initial glimpse of this complex materials landscape. Our particular approach involves keeping the volume fraction of the particle species of larger size constant while monitoring the effects that the gradual addition of particle species of smaller size has on both the static structures and the relaxation dynamics of the system.

From an experimental point of view, as a technique that probes statistically significant structural behaviors in the mesoscopic length scale range, small angle scattering has made significant contributions to the understanding of the static structure of colloidal dispersions that serve to validate the predictions made by theoretical calculations and numerical simulations.⁵⁰ On the dynamics front, dynamic light scattering (DLS), time-resolved confocal microscopy, and the recently emerged XPCS have played major roles in elucidating the equilibrium and nonequilibrium dynamics in a wide variety of colloidal dispersions^{51–58}. Among these techniques, DLS and XPCS share the same physical principles and monitor the

same physical quantity – time- and scattering-vector- dependent intensity fluctuation of coherent light. The main difference is that XPCS uses short wavelength X-rays in contrast to the visible light used in DLS. Because of this, the X-rays have superior penetrating power that overcomes the significant limitations imposed to DLS due to absorption or strong multiple scattering effects. XPCS, hence, has enabled studies impacting many material systems.

XPCS in the so-called ultra-small angle scattering (USAXS) regime, due to its scattering vector range bridging those of conventional DLS and pinhole-based XPCS, further makes possible direct detection of relaxation dynamics of larger (hundreds of nanometers to micrometer) colloids in aqueous environments due to the slower dynamics associated with their larger size and mass. Earlier realization of USAXS based XPCS was achieved using the high resolution and sensitivity offered by Bonse-Hart type crystal optics.⁵⁹ Very recently, a construction of a 30-meter SAXS instrument further enables XPCS detection in the USAXS regime for anisotropic scattering systems with better counting statistics.⁶⁰

In the following sections, we will first introduce the material systems and the experimental methods. We then present the theoretical background and the methods used for the reduction and analysis of the static and dynamic data, followed by detailed results and discussions. Finally, we offer concluding remarks.

Materials and techniques

Sample preparation

Monodisperse SiO₂ microspheres in dry-powder form were acquired from Bangs Laboratory, Inc., IN.^① (Product # SS03N/9757 and SS04N/10212) The mean, manufacturer-specified radii of these microspheres were 0.26 μm and 0.48 μm , respectively. The manufacturer-estimated coefficient of variation was between 10 % and 15 %. The manufacturer-specified mass density was 2.0 g/cm³.

The dry powders were aggregated. To disperse the microspheres, we developed the following protocol that was proven effective. First, we used a mortar and pestle to gently break apart the visible large aggregates. Then we weighed and added an appropriate amount of silica powder to a vial that contained the fluid of interest and repeated rigorous vortexing (60 s) and sonication using a sonic bath (30 minutes). Probe sonicators were found ineffective for this purpose. The number of repetitions was greater than 10. The dispersion of individual, non-aggregated microspheres was confirmed using dynamic light scattering measurements after further dilution.

For this study, the fluid of interest was a mixture of DI water and polyethylene glycol (PEG) (Sigma Aldrich) of molecular mass 2000 Da with a negligible amount of buffer solution. The mass ratio between DI water and PEG was 7:3. After mixing, the fluid was vortexed and left overnight before usage to ensure PEG was completely dissolved.

^①Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

To ensure sample consistency, we created two stock suspensions of monodisperse silica particles with 10 % volume and nominal radii at 0.26 μm and 0.48 μm , respectively. We then prepared single component and bimodal dispersions by mixing known volumes of single-component stock suspensions and diluting to achieve the desired sample composition. The list of samples is found in Table 1. The resulting dispersions were found stable without significant sedimentation after 12 h. In all cases, the dispersions appeared milky, making them unsuitable samples for light scattering measurements.

Experimental techniques

Small angle X-ray scattering experiments were conducted at the USAXS instrument at the Advanced Photon Source, Argonne National Laboratory.⁶¹ This instrument makes use of Bonse-Hart type crystal optics to access a scattering q range that is normally unavailable to a conventional pinhole-based SAXS camera. Here q is the magnitude of the scattering vector, and is defined as $q = 4\pi/\lambda \sin(\theta)$, where λ is the X-ray wavelength and θ is one half of the scattering angle 2θ . Coupled with pinhole SAXS measurements using an add-on Pilatus 100K detector, the USAXS instrument can routinely access a q range from $1 \times 10^{-4} \text{ \AA}^{-1}$ to $1 \text{ \AA}^{-1}$ with a q resolution of $\approx 1 \times 10^{-4} \text{ \AA}^{-1}$.⁶²

1D-collimated USAXS experiments were conducted in a stepping-scan mode using monochromatic 17 keV X-rays ($\lambda = 0.7293 \text{ \AA}$). The energy resolution E/E , where E is the nominal X-ray energy, is on the order of 10^{-4} . The beam size was $0.8 \text{ mm} \times 0.4 \text{ mm}$. The X-ray flux density was $\approx 10^{13} \text{ photon/mm}^2$. Each scan had 300 data points that were logarithmically distributed in the measured q range. The data collection time for each data point was 1 s. The samples were loaded into a 1.5 mm diameter quartz capillary (nominal wall thickness 0.01 mm) immediately after a brief vortexing treatment as a measure to ensure sample consistency. For both USAXS and XPCS experiments, the beam was centered on the vertically-placed capillary. We examined the samples after both USAXS and XPCS experiments and found no signs of radiation effects such as bubbling.

USAXS-based XPCS measurements were conducted using the same instrument with a different instrumental configuration to make use of the optical coherent properties of the partially coherent beam.⁵⁹ The instrument was configured in a 2D collimated geometry. The X-ray energy was set at 10.5 keV. The beam size was defined by two pairs of high-resolution JJ slits (JJ X-ray A/S, Hoersholm, Denmark) at $15 \mu\text{m}$ (horizontal) $\times 50 \mu\text{m}$ (vertical), a size that was previously determined to offer the best compromise between the coherent flux and the partial coherence of the beam.⁶³ It is worth noting that, unlike conventional area-detector-based XPCS setups that acquire coherent scattering intensities at many q s simultaneously, the coherent scattering data in a USAXS-based XPCS experiment were acquired using a scintillating (point) detector at 100 Hz at fixed q values. We set the total data acquisition time at least $20 \times$ the estimated dynamic time scale of the underlying equilibrium dynamics at each q , which was determined in trial experiments. The total measurement time for each q was at least 120 s.

To eliminate the effect that temperature fluctuation in the hutch has on the equilibrium dynamics, we set the sample capillary in a Linkam TH600 thermal stage (Linkam Scientific Instruments Ltd., Tadworth, UK) which uses both electrical resistive heating and liquid

nitrogen circulation to provide rapid heating and cooling. We set the temperature at 20 °C and the heating/cooling rate at 50 °C/min. We estimate that the temperature deviation from the thermocouple readout was ≈ 0.1 °C, and the temperature gradient in the sample was insignificant.

To visually examine the size, shape, and degree of aggregation of the silica powders, we made use of a JEOL JSM-7100F (JEOL, Ltd. Akishima, Tokyo, Japan) field-emission scanning electron microscope (SEM). The SEM was operated at 15 kV for secondary electron (SE) imaging.

Scattering theory

To facilitate discussion in this paper, it is worth reviewing the fundamental scattering theories of polydisperse, more specifically, bimodal colloidal dispersions under the Born approximation.

The microstructure of a colloidal system consisting of p species can be generally described by $p(p+1)/2$ radial distribution functions, $g_{ij}(r)$, which are proportional to the probability of finding a particle of species i at a distance r away from another particle of species j . Once the analytical or numerical form of the radial distribution function, i.e., microstructure, is known, macroscopic thermodynamic properties such as total energy, pressure, and isothermal compressibility can be readily calculated.

Scattering experiments offer the most accessible and perhaps most statistically reliable approach to study the complex microstructures of polydisperse colloidal dispersions in the *reciprocal* space (we confine the discussions hereafter to the case of X-ray scattering), where the scattering intensity for a p -component mixture is described by the following relation,

$$I(q) = \sum_{i,j=1}^p [n_i n_j]^{1/2} F_i(q) F_j(q) S_{ij}(q), \quad (1)$$

Here, $F_i(q)$ is the scattering form factor, n_i is the number densities of the i^{th} component, and $S_{ij}(q)$ denotes the partial structure factors accounting for the interparticle scattering interference between the i^{th} and j^{th} components of particles. Particularly, the scattering form factor is related to the particle geometry and its scattering amplitude f_i (scattering amplitude at $q = 0$), which depends on the volume of the colloidal particle V_i and the differences in the X-ray scattering length densities of the colloidal particle ρ_i and the solvent ρ_s , following,

$$f_i = V_i(\rho_i - \rho_s). \quad (2)$$

For a bimodal colloidal dispersion of components 1 and 2, Eqn. (1) can be broken down to three terms,

$$I(q) = n_1 F_1^2(q) S_{11}(q) + 2(n_1 n_2)^{1/2} F_1(q) F_2(q) S_{12}(q) + n_2 F_2^2(q) S_{22}(q). \quad (3)$$

In this form, the total scattering intensity can be described by the simple summation of self-scatterings from component 1 alone (first term), components 2 alone (third term), and the cross scattering between components 1 and 2 (second term). Due to the pairwise nature of the colloidal interaction, the approach to reduce Eqn. (1) to Eqn. (2) can be easily extended to many component systems with the introduction of relevant self-scattering and cross-scattering terms.

Assuming the system is rotationally invariant, the partial structure factors in Eqn. (3) can be related to the total correlation function $h_{ij}(r)$ following

$$S_{ij}(q) = \delta_{ij} + H_{ij}(q) = \delta_{ij} + (n_i n_j)^{1/2} \int_0^\infty 4\pi r^2 h_{ij}(r) \frac{\sin(qr)}{qr} dr, \quad (4)$$

where δ_{ij} is the Kronecker delta function, $H_{ij}(q)$ is the direct Fourier transform of the total correlation function. Here, the total correlation function is related to the radial distribution function following $h_{ij}(r) = g_{ij}(r) - 1$.

Solving the partial structure factors often involves the Ornstein-Zernike (OZ) equation, which separates the many-body effect into direct and indirect components by introducing a direct correlation function $c_{ij}(r)$. The OZ equation for a multiple component, an integral equation in real space, has a much simpler form in reciprocal space, with its matrix form following,

$$[\mathbf{I} + \mathbf{H}(q)] \{\mathbf{I} - \mathbf{C}(q)\} = \mathbf{I}, \quad (5)$$

where $\mathbf{I}$ is a unit matrix and $c_{ij}(q)$ is the Fourier transform of $c_{ij}(r)$.⁶⁴ To solve Eqn. (5), an addition equation, often known as the closure relation, is required.

One of the most commonly used closures is the so-called Percus-Yevick approximation, which is known to well describe particles with an impenetrable core. Under Percus-Yevick closure, for a multiple-component mixture, the radial distribution functions $g_{ij}(r)$ and the direct correlation functions $c_{ij}(r)$ are related following,

$$g_{ij} \left[\exp \left(-\frac{\phi_{ij}(r)}{\kappa_B T} \right) - 1 \right] = \exp \left(-\frac{\phi_{ij}(r)}{\kappa_B T} \right) c_{ij}(r). \quad (6)$$

Here, κ_B is the Boltzmann constant, T is temperature, and $\phi(r)$ is the pairwise potential between the particles.

The partial structure factors in a bimodal mixture system were given by Ashcroft and Langreth,⁶⁵ on the basis of the exact solution of the direct correlation functions by Lebowitz.³² Under the assumption that two components of a bimodal mixture are *exactly monodisperse* in size, the partial structure factors can be summarized into the following equations.

$$S_{11}(q) = \frac{1 - n_2 C_{22}(q)}{1 - n_1 C_{11}(q) - n_2 C_{22}(q) + n_1 n_2 C_{11}(q) C_{22}(q) - n_1 n_2 C_{12}^2(q)}, \quad (7a)$$

$$S_{12}(q) = \frac{n_1 n_2 C_{12}(q)}{1 - n_1 C_{11}(q) - n_2 C_{22}(q) + n_1 n_2 C_{11}(q) C_{22}(q) - n_1 n_2 C_{12}^2(q)}, \quad (7b)$$

$$S_{22}(q) = \frac{1 - n_1 C_{11}(q)}{1 - n_1 C_{11}(q) - n_2 C_{22}(q) + n_1 n_2 C_{11}(q) C_{22}(q) - n_1 n_2 C_{12}^2(q)}. \quad (7c)$$

It is clear from Eqns. 7(a–c) that the partial structure factors are only related to the direct correlation functions in reciprocal space. Further details of this classical treatment can be found elsewhere.^{22, 65–66} We also note that a suite of software programs that describes the bimodal structure factors listed above has been developed at NIST and is available upon request.

For a spherical colloidal particle with radius R , its geometrical particle scattering form factor is given by

$$F_i(q) = f_i \times 4\pi \int_0^R \frac{\sin(qr)}{qr} r^2 dr = V_i(\rho_i - \rho_s) \times \left[\frac{3(\sin(qR) - qR \cos(qR))}{(qR)^3} \right]. \quad (8)$$

In a bimodal spherical scattering system, under Percus-Yevick closure, the observed scattering intensity can be modeled using Eqn. (3), with the addition of Eqns. (7) and (8).

Results and Discussions

To examine the morphology of the as-received powder samples, we performed standard SEM measurements. A typical SEM image of the large silica particles is shown in Figure 1. It is clear from this image that the silica particles are largely spherical in shape, and are fairly monodisperse in size. It is also worth noting that SEM indicates that the particle radii are slightly smaller than 0.48 μm , the nominal radius specified by the manufacturer.

USAXS measurements provide a statistically representative characterization of the size distributions of both species of spherical particles used in this study. An important element of any scattering experiment is the scattering contrast of the components involved. The

calculated theoretical contrasts are shown in Table 2. This table demonstrates that despite the relatively large amount of PEG2000 that is present in the colloidal dispersions, its X-ray scattering contrast is very weak (about 1 %) compared with that of the silica colloidal particles. Therefore, the observed experimental scattering intensity predominantly originates from the silica particles and reflects the structures of the bimodal colloidal mixture, itself, in the presence of the short-chain PEG2000 molecules.

To determine the size distribution of the colloidal particles, we performed measurements on the monodisperse dispersions, namely, Sample A and Sample B. Their respective 1D-collimated USAXS data are shown in Figure 2. For these two samples, we performed the data reduction and analysis using the standard SAXS data analysis package *Irena*⁶⁷, developed at the APS. In order to eliminate numerical uncertainties introduced by the desmearing process⁶⁸, we opted to perform data reduction and analysis on the measured slit-smear data, which requires convolving the modeled intensity $I(q)$ with the known rectangular instrumental slit before fitting to the data. The size of the slit in q is determined by the wavelength, type of crystal optics, sample to detector distance, and the size of the photodiode detector.

Both scattering curves in Figure 2 show large numbers of Bessel oscillations that persist to the intermediate q regime. This characteristic strongly indicates that the silica particles are spherical in shape and have a narrow size distribution. Both curves also show a high q scattering plateau. This feature is related to the presence of nm-scale pore structure within the spherical particles. We have performed a further and separate study that investigates the ionic penetration in these colloidal particles, which confirmed the availability of pores that gives rise to this type of high q scattering. This result will be reported elsewhere. In addition, we did not observe any upturn at the very low- q range of the USAXS profiles, which indicates that the silica particles do not aggregate and remain well dispersed.

To extract the exact size distribution of the silica particles, we analyzed the scattering profile using the scattering form factor for spheres given by Eqn. (8) and assuming that the size of the particles follows a Gaussian volume size distribution, given by

$$\phi(r) = \phi_0 \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{(r - r_0)^2}{2\sigma^2} \right], \quad (9)$$

where ϕ_0 is the total volume of the silica particles, r_0 is the nominal radius, and σ is the Gaussian width.

When the size distribution is modest, it is known that an average scattering form factor could be calculated based on the size distribution to account for the effect of polydispersity⁶⁹. In simple mathematical terms, making use of Eqn. (8) and (9), we find the size-normalized scattering intensity in the following form:

$$I_0(q) = \int \left[\Delta\rho \frac{4}{3} \pi r^3 \left[\frac{3(\sin(qr) - qr \cos(qr))}{(qr)^3} \right] \right]^2 \times \frac{1}{\sigma \sqrt{2\pi}} \exp \left[-\frac{(r - r_0)^2}{2\sigma^2} \right] dr. \quad (10)$$

For a one-component isotropic moderately concentrated system, the form factor and structure factor contributions to the scattering are separable. Eqn. (3) can be further simplified to

$$I(q) = \frac{\varphi}{V} I_0(q) S(q), \quad (11)$$

where φ is the sample volume fraction and $S(q)$ is a single-component structure-factor representation. For the analysis that follows, we used a Percus-Yevick structure factor.

For this work, our primary focus is the interparticle structural behavior of the bimodal dispersions. Hence, we modeled the high- q scattering intensity using a Unified function⁷⁰, which, by coupling general scattering laws, provides a generic method of parameterization of the scattering curves. Making use of the high degree of flexibility of the Unified approach, we conducted a primitive characterization of the high- q scattering behavior.

Using a model that combines both a size distribution model (Eqn. (11)) and a Unified function, we performed a least-squares regression analysis to minimize the total errors and analyzed the scattering intensities profiles from the monodisperse dispersions. The fitting results are also shown in Figure 2 as solid lines. It is evident that the model describes the data very well, particularly the part of data concerning the low- q scattering characteristic of the overall colloidal particles. This result confirms that a Gaussian size distribution well describes the colloidal particles and validates the choice of Percus-Yevick structure factor, which suggests that the particles follow hard-sphere behaviors. As an example, the inset in Figure 2 shows the volume size distribution of larger spheres. We found that the mean radii for the larger and smaller colloids are 4330 Å and 2410 Å, respectively. Both sizes are smaller than the manufacturer-specified radii, which agree with the SEM observations. The difference may have to do with different size measurement techniques employed, as it is known that different techniques probe different physical properties that may lead to different sizing parameters⁷¹. The USAXS results, which are summarized in Table 3, indicate that the size distributions were found to have a full width at half maximum (FWHM) of 4.6 % and 6.2 % of the mean size for the larger and smaller colloids, respectively, confirming the existence of very narrow size distributions. This enables a simplification of the expressions for the overall scattering intensity from each particle population by assuming a small dispersion around a size-normalized scattering intensity.⁵⁰ Previous work has demonstrated that a broad particle size distribution can lead to significant challenges in determining and interpreting the scattering intensities from the density fluctuations intermediate between the mean particle sizes in mixed colloidal dispersions.^{22, 72} We confirm that such difficulties are avoided by incorporating the narrow size distributions found in the current study into a size-normalized scattering form factor. As an aside, our model also shows that the pores that give rise to the high- q scattering intensity have a mean radius of (20 ± 2) Å.

To examine the effect that gradual introduction of small colloidal particles has on the overall structure of a bimodal mixture, we performed USAXS experiments on the bimodal colloidal dispersions listed in Table 1. The slit-smeared experimental scattering intensity profiles are shown in Figure 3. With increasing the volume fraction of the small colloidal particles, we

observed a monotonic increase of the overall scattering intensity, as expected. More importantly, across the range of sample compositions, we did not observe a low- q upturn that is characteristic of particle aggregation. This is in stark contrast to the observations made in an earlier scattering study of bimodal hard-sphere mixtures of the same material (SiO_2 colloidal particles synthesized using the Stober method) and a very similar size ratio ($R_{\text{small}}/R_{\text{large}} = 0.51$).²² There, despite a general fluid-like behavior, a low volume fraction of aggregates existed and hence a third population whose nominal size is significantly greater than the diameters of the bimodal components had to be introduced.

In order to perform a quantitative analysis of the scattering intensity profiles of the bimodal dispersions and directly model the partial structure factors, it is necessary to work with the differential scattering cross sections. For this purpose, we desmeared the slit-smeared intensity using the well-established Lake method⁷³. This treatment recovered the differential scattering cross section and enables direct modeling and recovering of partial structure factors using Eqn. (3). This equation, however, was established for a bimodal dispersion with fixed sizes, i.e., both species are strictly monodisperse in size. To overcome this restriction, we accounted for the modest polydispersity in the particle size distributions of both species by calculating their size-normalized scattering intensities using the sizing parameters listed in Table 3, following Eqn. (10). We further assumed that the partial structure factor $S_{11}(q)$, $S_{12}(q)$, and $S_{22}(q)$ for monodisperse particles can be reasonably approximated for particles with narrow size distributions, which is a widely accepted practice.^{23, 69, 74} For our analysis, we adopted a simplest approach, where our model (Eqn. (3)) only includes the volume fractions of the large and small species, as well as a normalization factor that accounts for the uncertainties in the sample thickness. We made use of a least-squares regression analysis to minimize the total error by altering these fitting parameters in the range of $q < 0.01 \text{ \AA}^{-1}$, as it is most relevant to the structure of the dispersions. The volume fractions and their standard deviations obtained from the fits of the bimodal dispersions are listed in Table 4.

Figure 4 displays the desmeared experimental scattering intensity profile of Sample H, the sample with the highest combined volume concentration of colloids, and its corresponding model fit. From the data point of view, when compared with Figure 3, it is evident that the desmeared data have a higher degree of point-to-point scatter. While the Lake method solves the inverse problem by incrementally convolving the desmeared intensity using a known slit size until it recovers the starting slit-smeared data to within the specified data residuals, it inevitably introduces a numerical uncertainty that manifests itself in the form of the aforementioned point-to-point scatter. Still, as one can see, the agreement between the experimental data and the model results is satisfactory. The model is able to reproduce all the important features, including the oscillations, the heights, and depths in the total desmeared intensity curve. Within the experimental accuracy and the non-negligible uncertainties from both the experiments and the desmearing procedure, the agreement is quantitative as well. Fitting results for other dispersions, which are included in the Supplementary Materials, also exhibit similar behaviors. Based on this result, we conclude that the model well describes the structure behavior of this class of bimodal colloidal dispersion and the bimodal dispersions in the current study are hard-sphere in nature.

To elucidate the impact that the addition of small colloidal particles has on the overall structures of the bimodal dispersions, it is important to examine the partial structure factors that are determined by the potential of mean force (effective pair interaction potential that reproduces the radial distribution function). We calculated the partial structure factors using the fitting parameters summarized in Table 4. The partial structure factors $S_{11}(q)$, $S_{12}(q)$, and $S_{22}(q)$ are shown in Figure 5.

It is clear from Figure 5 that when no small colloidal particles were introduced, a simple one-component hard sphere structure factor was recovered by $S_{11}(q)$, with both $S_{12}(q)$ and $S_{22}(q)$ being zero. The gradual addition of the smaller colloidal particles also does not introduce strong interaction peaks in $S_{22}(q)$. Its deviation from 1 is relatively insignificant. The cross term $S_{12}(q)$, on the other hand, shows appreciable departure from 0, especially at low q values. Last, the partial structure factor $S_{11}(q)$ appears to be the least affected, which suggests that the perturbation to the large-large colloid interaction is modest. However, the maximum position of the first peak in $S_{11}(q)$ does shift to higher q with increasing the volume fraction of small colloidal particles, which indicates that the average separation distance between neighboring large spheres gets further “squeezed” with the gradual addition of small colloidal particles. When compared with an earlier study of charge-stabilized perfluorinated (PFA) and polystyrene (PS) bimodal colloidal dispersions of a similar total volume fraction and an almost identical size ratio^{15–16}, we found that the magnitude of the structure factor undulations in our study is significantly less, which can be attributed to the much stronger Coulombic interparticle interactions experienced between PFA and PS particles.

Another interesting aspect is the positioning of the principal peaks. It is evident that the first peak of $S_{11}(q)$ lies closer to $q = 0$ than that of $S_{22}(q)$, with the first peak of $S_{12}(q)$ in the middle between them. In real space terms, this means that the primary separation distance between the larger particles is always greater than that between the smaller particles, with the large-small separation distance being intermediate. This is in contradiction to the prediction made by the classic substitutional model by Faber and Ziman⁷⁵, where all the particles in a multiple-component liquid are considered to be identical from an interaction point of view, i.e., such a liquid can be approximated as a single component liquid. In a bimodal system such as the one investigated in this study, this approximation inevitably leads to all three partial radial distribution functions being identical. While the substitutional model was found to describe the experimental findings in selected bimodal dispersions,^{76–77} the clear differences in the partial structure factors found in this work makes it evident that local ordering of the two species of particles does not resemble that of a one-component macrofluid.

An important feature shown in Figure 5 is that all the bimodal dispersions possess homogenous liquid-like orders. The existence of fluid-fluid phase separation in bimodal sphere dispersions is a long standing question. Whereas the Percus-Yevick approximation predicts that hard spheres would always mix at all dispersion states for any size ratio between the particle species,⁷⁸ improved integral equation studies suggest that the entropic depletion effect can cause spinodal instability in the bimodal dispersions and lead to a demixing transition.^{30, 79} In this case, analogous to classical colloid-polymer mixtures,⁸⁰

clustering of large spheres makes more free volume available for the small ones, which in turn could give rise to an increase of the total system entropy. Such clustering (or aggregates) of larger colloids was observed not only in bimodal dispersions with high size ratios ($R_{\text{large}}/R_{\text{small}} \sim 5$)²³, but also in dispersions with more moderate size ratios ($2 < R_{\text{large}}/R_{\text{small}} < 3.7$)^{22, 81}. In our systems, despite its relatively high particle concentrations and the presence of small particle species and low molecular weight polymers, no fluid-fluid phase separation is observed. Both species of particles remain well mixed through the phase space that was explored. This result agrees with the phase diagram predicted for bimodal hard-sphere dispersion, albeit the presence of polymers was not considered in the theoretical predictions.

From the thermodynamics point of view, one important conclusion that could be drawn from the partial structure factors is the isothermal compressibility, which is related to the behavior of $S(q)$ as $q \rightarrow 0$, a q regime where USAXS has an inherent advantage over conventional pinhole SAXS instruments. For a bimodal dispersion, the general, potential-independent isothermal compressibility χ_T can be acquired following the Ornstein-Zernike fluctuation formulation as,

$$\rho k_B T \chi_T = \frac{S_{11}(0)S_{22}(0) - S_{12}^2(0)}{x_1 S_{22}(0) + x_2 S_{11}(0) - 2\sqrt{x_1 x_2} S_{12}(0)}, \quad (12)$$

where $\rho = (N_1 + N_2)/V$, $x_1 = N_1/(N_1 + N_2)$, $x_2 = N_2/(N_1 + N_2)$, N_1 , N_2 , k_B , and T are the total number of large colloidal particles, small colloidal particles, Boltzmann constant, and absolute temperature, respectively.

Figure 6 shows the dimensionless isothermal compressibility $\rho k_B T \chi_T$ for the bimodal dispersions as a function of the volume fraction of the small colloidal particles. It is evident that when the number density of the small colloidal particles is comparable to that of the large one, its perturbation to the overall compressibility is insignificant. However, when the small particles significantly outnumber the large particles, their placement in a homogeneous fluid exerts additional pressure on the large particles, hence leading to a less compressible fluid. This result is in qualitative agreement with an earlier theoretical investigation of a bimodal mixture of particularized polymer and colloids, where the addition of small polymers was also found as the deciding factor in determining isothermal compressibility.⁸²

To assess the effect that gradual addition of small colloidal particles has on the overall dynamics of the dispersions, we performed USAXS-based XPCS experiments. For a system that undergoes equilibrium dynamics, typical of colloidal dispersions, XPCS probes the dynamic properties by measuring the temporal correlation of the coherent scattering intensity, which yields the characteristic time scales of the corresponding relaxation processes. The intensity autocorrelation function is defined as,

$$g_2(t) = \frac{\langle I(t+t')I(t') \rangle_T}{\langle I(t') \rangle_T^2}, \quad (13)$$

where $I(t)$ is the integrated scattering intensity in an interval Δt around a time t , and the angular brackets in Eqn. (13) denote a time average, which for ergodic systems is equivalent to an ensemble average. To extract the relaxation time scales, we further analyzed $g_2(t)$ using the so-called Kohlrausch-Williams-Watts (KWW) function, a function that is widely used in the analysis of XPCS data. This function is defined as,

$$g_2(t) = \beta \exp \left(-2 \times \left(\frac{t}{\tau} \right)^\gamma \right) + 1. \quad (14)$$

Here, β is the Siegert factor that is related to the experimental geometry and the beam coherence, γ is the Kohlrausch exponent, and τ is the characteristic relaxation time. For these particular datasets, the detailed data reduction and analysis procedures have been reported previously.⁵⁹ We found that the KWW function describes $g_2(t)$ very well. The dependences of τ on q for two representative samples (Sample A and Sample H, the samples with the least and the most amount of small colloidal particles) are shown in Figure 7(a).

It is clear from Figure 7(a) that both $\tau(q)$ curves monotonically decrease as the value of q increases, which indicates that faster dynamics are associated with larger scattering vector q or smaller mean travel distance. This behavior is expected given that, under normal circumstances, short-distance fluctuations occur more rapidly than their long-distance counterparts and agrees with many previous observations of colloidal dispersions.^{23, 69} We also observed a general trend that, across the q range, at each specific q , the dynamic time scale steadily increases monotonically with increasing the volume concentration of the small particles ($\tau(q)$ curves of Samples B to G are reported in the Supplemental Materials). Intuitively, this observation makes physical sense as the additional small particles inevitably lead to a higher bulk viscosity through hydrodynamic interactions, thus increasing the dynamic time scales. While this result agrees with predictions for a simple colloidal dispersion (without presence of polymer), it is different from a recent report by Poling-Skutvik *et al.* where particle dynamics in semidilute polymer solutions within a range of mass fractions of monodisperse SiO₂ particles from 1 % to 10 % were found to be similar in time scales.⁴² A monotonic dependence of the dynamics time scale on the silica volume fraction was also found to be absent. These observations were attributed to the good dispersity of the colloids and the polymers being Gaussian coils. One major difference between the Poling-Skutvik study and ours is the molecular weight of the polymers. The PEG in our study has a nominal molecular mass of 2000 Da, whereas the polystyrene used in the Poling-Skutvik study has a weight-averaged molecular weight of 706 kDa. We surmise that the observed difference in the monotonicity may have to do with the entanglement effects of the polymers that serve to damp the hydrodynamic interactions, an effect that is much more prominent when the molecular weight of polymers is large. The exact role of the molecular weight of the polymers on the particle dynamics in reasonably concentrated colloidal dispersions may require further experimental and theoretical elucidations.

For colloidal dispersions, the effective relaxation rate could be described by $\Gamma = q^2 D(q)$, where $D(q)$ is a wave-vector dependent, effective diffusion constant that describes the

diffusion of interacting particles.^{83–84} The relation rate Γ is related to the relaxation time scale following $\Gamma = \tau^{-1}$. Therefore, the ratio between D_0 , the diffusion constant for a single particle undergoing Brownian motion in the same medium under the same conditions, and $D(q)$ follows a simple relationship of $q^2\tau$. Figure 7(b) shows the dependence of $q^2\tau$ dependency on q for Sample A, the dispersion that only has large colloidal particles. It is clear that the inverse of the effective diffusion coefficients displays a peak that greatly resembles the primary peak in the single-component static structure factor, as shown in Figure 5(a). This effect, normally referred to as de Gennes narrowing, shows that the wave vector dependence of the interparticle diffusion coefficient is inversely proportional to the interparticle structure factor. In other words, the rate of interparticle motion is inversely proportional to the probability distribution of the spatial configuration of particles in a single-component colloidal dispersion. It is worth noting that de Gennes narrowing has been used to indicate collective motions of colloidal particles in both unconfined and confined fluids.^{69, 85–86} For bimodal dispersions, due to the complications introduced by the partial structure factors, the de Gennes-narrowing type analysis no longer applies. Still, the empirical KWW exponent γ is greater than 1, again indicating that the motions of the colloidal particles are at least partially collective in nature,⁶⁹ possibly due to the hydrodynamic interactions.

A close examination of Figure 2 reveals that, when $q = 0.0004 \text{ \AA}^{-1}$, due to their larger size, the larger colloidal particles have significantly higher scattering power when compared with the smaller particles. This scattering power comparison can also be translated to the XPCS case, which provides an opportunity to use the larger particles as a probe to approximately evaluate the effects of the addition of smaller particles on the overall viscosity of the dispersions. Following the Einstein-Stokes equation, $D = k_B T / 6\pi\eta R$, as well as the established relationship between the effective dynamic time scale and the diffusion constant, $1/\tau = Dq^2$, we obtain an expression for the effective viscosity η_{eff} , described as $\eta_{\text{eff}} = q^2 k_B T \tau / 6\pi R$. Here R is the nominal large sphere radius.

Figure 8 shows the effective viscosity η_{eff} as a function of the volume fraction of the small colloidal particles. It is clearly demonstrated that the addition of the small particles leads to an increase in the overall dynamic viscosity. We further calculated the theoretical dynamic viscosity of a single component dispersion of hard spheres of the same total volume fraction, also shown in Figure 8 as the red dashed curve. Evidently, when the volume fraction of the small particles is low, the experimental and theoretical viscosities show good agreement. However, as the number density of the small particles grows significantly larger than that of the large particles, the single-component viscosity model fails to describe the experimental observation. This result indicates that even in a homogeneous bimodal hard-sphere-like colloidal dispersion, the mutual interactions between the small particles and large particles, described by the partial structure factors, serve to significantly alter the bulk dynamic properties of the bimodal dispersions.

Concluding Remarks

In this paper, we have presented a systematic investigation of a series of bimodal colloidal dispersions in a low-molecular weight PEG solution by using synchrotron USAXS and

USAXS-based XPCS. By fixing the volume fraction of the large particles and gradually increasing the volume fraction of the small particles, we studied the effects that the additional small particles have on the equilibrium structure and dynamics. Compared with light scattering techniques, which suffer from optical opaqueness due to multiple scattering, the X-ray scattering techniques used in this study avoid this problem and present a unique window for static and dynamic structure characterization.

The USAXS measurements on the individual colloidal dispersions proved that both types of silica spheres have a high degree of monodispersity in size. We found that, when taking into account the size distributions of the particles, the partial structure factors can be satisfactorily described for the bimodal colloidal dispersions using a Percus-Yevick bimodal hard sphere potential. From the partial structure point of view, we found that although the partial structure factors between the small particles and between the large and small particles change substantially with increasing volume fraction of small particles, the partial structure factor between the large particles does not exhibit significant variation; this suggests a modest perturbation to the large-large colloidal interaction. Further analysis of the partial structure factors shows that the bimodal colloidal dispersion is homogeneous without the aggregation of large spheres that is commonly observed in similar bimodal systems. We also calculated the isothermal compressibility of the bimodal colloidal dispersion and found that the dispersion becomes less compressible with an increasing proportion of small colloidal particles.

On the dynamics side, the analysis of the XPCS data showed that for each dispersion, the q -dependent dynamic time scale decreases monotonically with increasing q , revealing more rapid short-distance fluctuations than long-distance fluctuations. A monotonic increase in the overall time scale curve was also observed with increasing volume fraction of small particles. For the single-component large-particle dispersion, we found that the inverse of the effective diffusion coefficient shows a peak when plotting against q . This peak resembles the primary peak in the static structure factor and suggests that the rate of interparticle motion is inversely proportional to the probability distribution of the spatial configuration of particles. Finally, we compared the effective dynamic viscosity with theoretical predictions made for single-component colloidal dispersions with the same total volume fraction. This comparison shows significant departure when the number density of the small particles is large compared with that of the large particles, which indicates that the complex mutual interactions between large and small particles have a strong effect on the dynamic behavior of bimodal dispersions.

One other important aspect of this study is that the suspending medium is water-based. Despite the obvious importance of aqueous solutions, dynamic characterization of aqueous colloidal suspensions using XPCS has proven difficult, largely due to the very fast (ns – ms scale) dynamics associated with the equilibrium relaxation of nanoscale colloidal particles. Because of this challenge, many existing studies of colloidal dynamics are limited to highly viscous suspending media such as glycerol. USAXS-based XPCS provides access to a q range that is suitable to probe the dynamics of large micrometer-sized colloids whose dynamics are inherently slow. This characteristic of USAXS-based XPCS enabled the current study, despite the fact that the aqueous solution of PEG used in this study has a

dynamic viscosity approximately two orders of magnitude lower than that of glycerol. We acknowledge that the completion of this study has not been without challenges, mostly due to the counting statistics resulting from the low coherent flux and the short counting time required to probe the dynamics, which, to a large extent, created an undesired degree of uncertainty. This has prevented more quantitative conclusions from being drawn at this time. However, it is worth pointing out that the multi-bend achromat (MBA) storage ring upgrade that is widely being implemented and considered in the worldwide synchrotron community can potentially increase the coherent X-ray flux by 100 to 1000 times and improve the XPCS time resolution to 1 μ s. This dramatic improvement will enable X-ray scattering experiments to fully characterize the structural and dynamical behaviors of aqueous polydisperse colloidal dispersions and provide answers important to the understanding of complex colloidal behaviors of great relevance to the biological and environmental sciences.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
SEM image of the as-received 0.96 μm silica particles (nominal radius = 4800 $\text{\AA}$).

Figure 2.

The scattering curves show the slit-smear USAXS scattering profiles for the monodisperse colloidal dispersions Sample A and Sample B. The measurement uncertainties are smaller than the symbol sizes. The solid lines show the results from least-squares regression analysis using a model described in the text. The inset gives an example of the volume size distribution of the large colloidal particles in Sample A. Uncertainty in the data henceforth is smaller than the symbol sizes.

Figure 3.

Experimental slit-smeared scattering intensity profiles for the bimodal mixtures. All the mixtures contain 5 % volume large colloids. From Sample C to H, in sequence, the volume fractions of the small colloids are 0.5 %, 1 %, 2 %, 3 %, 4 %, and 5 %, respectively.

Figure 4. Experimental scattering intensity profile (after desmearing) of Sample H and model fit using the model described in Eqn. 3 – 10. The volume fractions for both species of colloids are 5 %.

Figure 5.

Calculated partial structure factors $S_{11}(q)$, $S_{12}(q)$, and $S_{22}(q)$ using the fitting parameters listed in Table 4.

Figure 6. Dimensionless isothermal compressibility $\rho k_B T \chi_T$ for the bimodal dispersions as a function of the volume fraction of the small colloidal particles, obtained from the partial structure factors $S_{11}(0)$, $S_{12}(0)$, and $S_{22}(0)$.

Figure 7.

(a) shows the relaxation time τ as a function of q for Samples A and H, as obtained from KWW fits of the autocorrelation function of the XPCS data. (b) The un-normalized $D_0/D(q)$ for sample A which demonstrates de Gennes narrowing.

Figure 8.

A comparison between the experimental effective viscosity of the colloidal dispersions and the normalized theoretical viscosities.

Table 1

List of samples and their preparation conditions.

Sample identifier	1 μm sphere (% vol)	0.5 μm sphere (% vol)
A	5	0
B	0	5
C	5	0.5
D	5	1
E	5	2
F	5	3
G	5	4
H	5	5

Table 2

Calculated scattering length density and scattering contrast

	Mass density (g/cm ³)	X-ray scattering length density (10 ¹⁰ cm ⁻²)	Scattering Contrast to solution (10 ²⁰ cm ⁻⁴)
SiO ₂	2.0	16.95	51.98
H ₂ O	1.0	9.42	
PEG	1.13	10.50	0.57
PEG + H ₂ O solution	1.04	9.74	

Table 3

Particle size determination using SAXS

Sample identifier	SAXS radius (Å)
A	4332 ± 198
B	2410 ± 150

Table 4

volume fraction of the large and small colloids in the bimodal mixtures as determined by SAXS analysis.

Sample identifier	Large sphere volume fraction	Small sphere volume fraction
	(% vol)	(% vol)
C	4.91 ± 0.60	0.62 ± 0.09
D	4.87 ± 0.50	1.14 ± 0.13
E	4.90 ± 0.41	1.98 ± 0.16
F	5.12 ± 0.42	3.04 ± 0.16
G	4.93 ± 0.51	3.88 ± 0.24
H	5.08 ± 0.42	4.75 ± 0.21