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Ultra-small-angle scattering studies of complex fluids

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Abstract

Recent experimental results from ultra-small-angle neutron and X-ray scattering (USANS and USAXS) studies of complex fluids, including colloidal dispersions, colloidal glasses, polymer blends, and biopolymer gels, are reviewed. We focus on data analysis and interpretation in the low q regime. New notable results include the apparent existence of large-scale structure in attractive colloidal glasses, the discovery of new morphological transitions in polymer blends via USANS, and the detection of micron-scale water channels in biopolymer gels.

Keywords: USANS; USAXS; Scattering; Multiscale materials; Colloidal glasses; Attractive glasses; Fractals; Polymer gels; Biomaterials; Polymer blends

1. Introduction

The fields of self-assembly and advanced materials are moving towards multiscale systems—materials, gels, and solutions that exhibit hierarchical structure on length scales ranging from nanometers to microns. To characterize the structure of these materials, a combination of techniques is necessary. A traditional approach is to combine information from light scattering, neutron or X-ray scattering, and microscopy. However, advances in instrumentation [1] have allowed for the development of ultra-small-angle scattering techniques (USAS), which probe larger length scales than conventional SANS and SAXS experiments. Current ultra-small-angle neutron scattering (USANS) instruments can probe length scales as large as 5 μm, and new instrument designs are being proposed which would extend this range to 50 μm [2].

USANS and ultra-small-angle X-ray scattering (USAXS) offer several advantages over light scattering and microscopy for characterizing micron-scale structure. They can be easily applied to concentrated opaque systems. Moreover, unlike some microscopy techniques, there is little risk of distorting the microstructure during sample preparation. USAXS instruments have been in operation since 1965; USANS instruments have been available since the mid-1990s [3] with several recent advances in instrument design [4,5]. However, these techniques are still somewhat underutilized in the general complex fluids community, due in part to questions over data interpretation. In this review, we intend to demonstrate the utility of USANS and USAXS by focusing on recent results for colloidal and polymeric materials, with an emphasis on data analysis and interpretation. As excellent reviews have appeared recently on USAS studies of colloidal crystals [6•] and complex materials such as composites and geomaterials [7••], we concentrate on solutions, gels, and glasses.

2. Colloidal dispersions and colloidal materials

2.1. Dilute solution interactions

USAS techniques allow for precise measurement of the scattered intensity as $q \rightarrow 0$. Because the structure factor at $q=0$ is related to the osmotic compressibility, spectra taken at low q can be used to determine interparticle interactions or test new models for interparticle potentials. An excellent example is the work of Lutterbach et al. [8] who used

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USAXS to probe the structure of binary mixtures of polystyrene (PS) and perfluoroalkoxy-copolymer (PFA) particles with diameters of 79 and 162 nm, respectively, at total volume fractions of roughly 9% in water. The partial structure factor of the PFA particles shows a peak that weakens and shifts to higher q as the small particles are added. In addition, there is an increase in the intensity at low q. All experimental data were found to agree with calculations for the structure factor computed using the repulsive portion of the DLVO potential with the hypernetted chain closure. This work represents the first comparison to theory of partial structure factors in a binary colloidal dispersion. A similar analysis was performed by Lynnard et al. [9•] and Reus et al. [10] who performed USAXS on single-component dispersions of bromostyrene lattices in conjunction with osmotic pressure measurements. They fit the experimental structure factors, using predictions from the DLVO potential to determine the effect charge on the latex particles.

As an intermediate between charged colloids and polyelectrolytes, Ohshima et al. [11•] considered USAXS from charged poly(amido amide) dendrimers with radii of 2–7 nm in aqueous solutions. These dendrimers were found to be weakly attractive in the presence of added HCl and strongly attractive when H_2SO4 was added. Thus, solution interactions were mediated by both the effective charge density and the charge number of counterions. By contrast, with charged colloids, where only the effective charge is important. The microstructure of these solutions has been proposed to be coexistent between ordered and disordered regions. However, the USAXS data did not show an upturn at low q, showing no clear distinction between ordered and disordered regions at length scales up to 8 μm.

2.2. Colloidal gels

It is well-known that attractive colloids can aggregate to form mass fractals, where the fractal dimension can be probed via low q scattering [12]. For such systems, the scattered intensity scales as $I{\sim}q^{-d_f}$ in the low q regime. The fractal dimension d_f must lie between 1 and 3 to be physically meaningful, and typical values for fractal colloidal aggregates are in the range 1.8–2.2, depending upon the mechanism for aggregation [12,13]. Until the advent of ultra-small-angle techniques, these types of measurements were performed using light scattering and, in some cases, SAXS. However, USAXS and USANS allow for the determination of fractal dimensions for opaque systems and fractals with large primary particles. Data from these systems are often fit using Beaucage's model [14••] for systems with arbitrary fractal dimension. This model contains a Guinier-type term added to a power law in q which describes the fractal dimension. It can be extended to systems with several structural levels by using a series of Guinier and power law terms, each describing different levels and length scales of structure. Another option for systems that show a correlation peak in the SAXS/SANS regime and power law scattering at lower q is to simultaneously fit data from SANS/SAXS and USAS by using a liquid-like structure factor and spherical form factor with an added term to describe the power law scaling at low q; for example, $I(q){\sim}P(q)S(q)+I_o q^{-d_f}$.

There is a large literature on scattering from fractals; we highlight two USAS studies of interest. USAXS has been utilized to study precursors to the growth of silicalite crystals [15•]. Amorphous colloidal silicalite with a characteristic size of 7 nm was first formed; these particles then aggregated. In some cases, a population of crystals was formed, resulting in a low q slope of about −4; in other cases, a fractal aggregate with d_f=1.8 was formed. Data were fit using an exact structure factor for mass fractals [16]. Muzny et al. [17] used SANS and USANS to examine fractal colloidal silica gels that were subjected to shear during gelation. Unsheared gels showed no excess scattering at low q, while sheared gels had a broad peak in the USANS spectra. The combined SANS/USANS spectra were fit with the expression $I(q)=I_o S_1(q)+P(q)S_2(q)$, where $P(q)$ is the form factor for silica spheres, $S_2(q)$ is a liquid-like structure factor, and $S_1(q)$ is an empirical relation of the form

$$S_1(q) = \frac{\left[\frac{\alpha}{1-\alpha} + 2\left(\frac{q\xi}{2\pi}\right)^{d_f}\right]}{\left[\frac{1}{1-\alpha} + \left(\frac{q\xi}{2\pi}\right)^{2d_f}\right]} \quad (1)$$

where α is the low q limit, $1/\xi$ is the position of the correlation peak, and $-d_f$ is the power law exponent. Using this model, the authors found ξ=2300 nm and d_f=2.9. Thus, the gels appear to densify when sheared during gelation.

2.3. Attractive and repulsive glasses: unexpected scattering at low q

Colloidal gels and glasses can exhibit similar rheological properties and dynamics, making them difficult to distinguish experimentally [18•]. However, there are key structural differences. In colloidal gels, attractive forces dominate, leading to an "open" percolated structure characterized by a fractal dimension d_f, as mentioned above. Colloidal glasses can form from either repulsive or attractive particles; however, repulsive forces are dominant and lead to slowing of the dynamics. The microstructure is much denser and more "crowded" than in a fractal colloidal gel, and the expectation is that $S(q)$ should have no characteristic features at low q [18•]. This behavior has been verified experimentally for colloidal glasses of repulsive particles, also referred to as "repulsive glasses." For example, Bonn et al. [18•,19], Knaebel et al. [20], and Bhatia et. al [21] examined repulsive isotropic glasses of

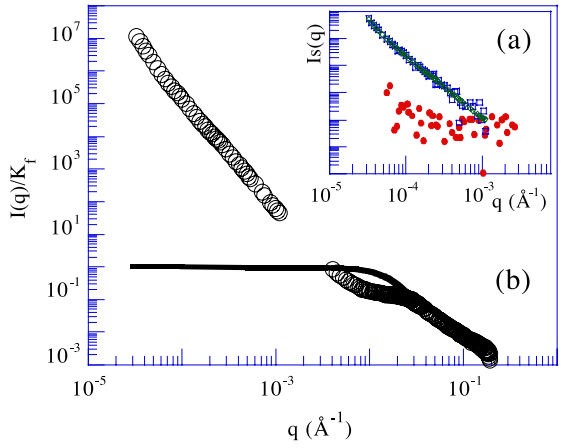

Fig. 1. (a) USANS data prior to desmearing for an isotropic repulsive glass (c=2.5 wt.%, •) and nematic gel (c=6 wt.%, □) of laponite particles [21]. Note the lack of features in the low q regime for the repulsive glass. ◇ are fit to the smeared data at 6 wt.%. (b) Normalized and corrected USANS and SANS data for c=6 wt.%, with form factor for disks (solid line).

laponite, an anisotropic clay, and found no q dependence of $S(q)$ in the low q regime with light scattering [19,20] and USANS [21]. Our data on isotropic glasses is shown in Fig. 1 and is compared to spectra from nematic laponite gels at higher concentrations, which display a q^{-4} dependence in the USANS regime [21].

However, it appears that glasses formed from attractive particles, referred to as "attractive glasses," do exhibit excess scattering at low q. Typically, the scattered intensity is found to scale as $q^{-\beta}$, with β between 3 and 4. These exponents are too large to indicate a mass fractal; rather, they are characteristic of "surface scattering" from compact objects with fractally rough surfaces. The limit of 4 corresponds to an object with a smooth distinct interface. An example is the work of Shah et al. [22••], who used USAXS to examine dense colloidal silica with a radius of 59 nm at volume fractions ϕ of about 0.40 with a polymer-induced depletion attraction. Their data showed a power law dependence of $I{\sim}q^{-3.5}$ in the low q range, which they interpret as the formation of dense aggregates of several particles. These aggregates are likely to have fractally rough surfaces, to be highly polydisperse, and to be interpenetrating to some degree [22••]. To interpret their data, they use a Debye–Büche (DB) function in the low q range:

$$S_{DB}(q) = \frac{48\phi(\xi/d)^3\langle\eta^2\rangle}{\left(1+q^2\xi^2\right)^2} \tag{2}$$

where d is the particle diameter, $\langle\eta^2\rangle$ is a dimensionless fluctuation parameter, and ξ is the correlation length. A length scale of 0.5–1.0 μm was found for the aggregate size, corresponding to 5–8 d. Neither the aggregate size nor low q exponent was found to depend systematically on the strength of attraction or particle size [22••].

Pontoni and Narayanan [23] also performed USAXS on an attractive glass of colloidal silica in a mixed solvent of 2,6-lutidine and D_2O. The particles exhibit a short-range attraction that increases as temperature increases. Below the glass transition, no low q excess scattering is observed, while above the glass transition, $I{\sim}q^{-4}$, again corresponding to formation of large clusters. The intensity over the entire q range for their combined SAXS and USAXS data was fit using Debye–Büche term for the low q range added to a spherical form factor and adhesive hard sphere structure factor for the mid-q range:

$$I(q) = P(q)S(q) + \frac{I_o}{\left(1+q^2\xi^2\right)^2} \tag{3}$$

Cluster sizes in the range 8–10 μm were obtained from these fits.

Recently, we performed USANS on spherical micelles of poly(styrene)–poly(acrylic acid) (PS–PAA) [24,25]. We have shown previously that these micelles form an attractive glass [26] where the strength of attraction is related to the degree of hydrolysis of the PAA block f. We also find that the low q scattering scales as $I{\sim}q^{-\beta}$, with β approximately 3–4 (Fig. 2). We believe this to be due to compact aggregates larger than 10 μm in size with fractally rough surfaces. Moreover, the exponent β was found to vary systematically from 3.8 to 2.9 as the strength of attraction increases. We verified the presence of these aggregates with fluorescence microscopy and found that they are highly polydisperse [25], as predicted by Shah et al. [22••]. Thus, USANS and USAXS studies have demonstrated that attractive colloidal glasses do indeed exhibit large-scale structure, and the interface of these aggregates appears to

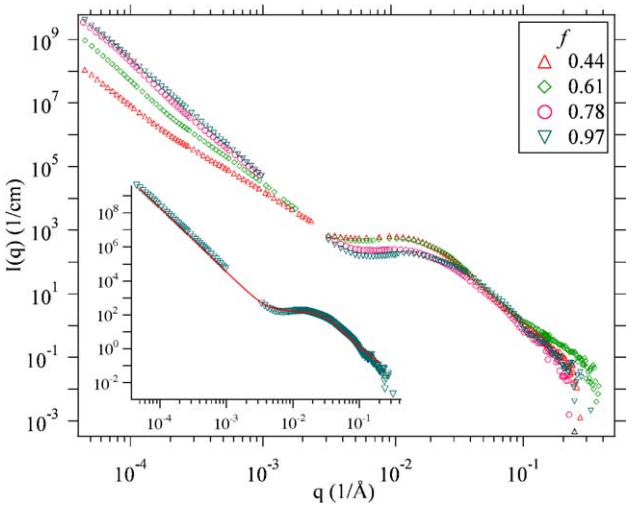

Fig. 2. Combined USANS and SANS spectra for attractive glasses of PS–PAA micelles [24,25] with differing degrees of hydrolysis f. Spectra are shown for a series with decreasing strength of attraction, from strongly attractive (f=0.44) to weakly attractive (f=0.97). The inset shows a sample fit to the combined SANS/USANS data.

becomes fractally "rougher" as the strength of attraction increases.

3. Polymeric and amphiphilic systems

3.1. Polymer blends

USAXS and USANS can be used to settle long-standing morphological questions as well as uncover new morphological transitions in polymer melts and blends. A series of papers by Agamalian et al. [27•,28] utilized USANS to observe blends of high-density linear polyethylene (HDPE) with highly branched hydrogenated polybutadiene (HPB) and low-density polyethylene (LDPE). The scattered intensity at low q was found to be six orders of magnitude lower for the HDPE/LDPE blend as compared to HDPE/HPB, suggesting that HDPE/LDPE does not microphase separate, resolving earlier questions about the melt miscibility of HDPE and LDPE. By contrast, the HDPE/HPB blend appeared to have micron-size inhomogeneities. To represent this, the data were fit to the model of Sabine and Bertram:

$$I(q) \sim \sum_{n=1}^{10} \left(\frac{b^n}{n^m} \right) \left[1 + \frac{q^2 R^2}{n^m} \right]^{-2} \quad (4)$$

Here, m=1.58, b is related to the average number of scattering events, and R is the average radius of the domains, found to be approximately 3.1 μm [27•].

A striking example of the utility of USANS in confirming new morphologies and morphological transitions is given by Lee et. [29••], who examined highly immiscible blends comprising polyisobutylene (PIB) and poly(isoprene) (PI), stabilized by a polypropylene (PP)–PE block copolymer surfactant. For a particular blend, clear phase separation was observed above 160 °C, with $I \sim q^{-4}$ over the q range probed by SANS. Below 160 °C, SANS shows no clear evidence of periodic microstructure. However, USANS shows a broad shoulder at q=0.01 nm^{-1}, with a q^{-3} dependence at lower q. The data are consistent with a bicontinuous microemulsion-to-macrophase separated transition at 160 °C, which had not previously been observed in polymer blends [29••]. Moreover, unlike lamellar or droplet microemulsion phases, biocontinuous phases are extremely difficult to image via TEM. Thus, USANS was crucial to the discovery of this morphological transition.

3.2. Polymer solutions and gels

Most USAXS and USANS studies on polymer solutions and polymer gels, including the dendrimer [11•] and PS–PAA systems [24,25] mentioned above, involve charged polymers. Such systems show an upturn in the scattered intensity at low q in conventional SANS and SAXS studies, indicating some large-scale structure. An early USAXS study performed by Li et al. [30] on sulfonated polystyrene shows that the low q scattering follows a power law, with exponents ranging from −2.4 to −3.6. Inasmuch as this range does not make sense physically for either mass fractals or surface scattering, the authors caution against interpreting these numbers as fractal dimensions [30]. Power law behavior can also be obtained from a power law distribution of polydisperse spheres, rods, or platelets [31]. Thus, the authors suggest that there are inhomogeneities present that are very irregular and highly polydisperse, perhaps ranging from nanometers to microns in size [30]. The low q slope was not dependent on ionic strength, the nature of the cations, or annealing conditions. Similar behavior was observed by Gebel and Lambard [32], who performed USAXS on water-swollen Nafion membranes. Low q exponents in the range of −1 to −4 were observed [32].

Takeshita et al. [33•,34,35] performed USANS on aqueous systems of fully saponified atactic poly(vinyl alcohol) (PVA) during gelation. Light scattering from these systems is consistent with a spinodal decomposition-type phase separation in the early stages of gelation. After macroscopic gelation, a broad peak appears in the USANS spectra, indicating well-defined domains with a size of 0.5–2.0 μm. The size of these domains grows as gelation proceeds, although the growth does not follow predictions from existing scaling theories. Note that these PVA systems do not show power law behavior at low q, only the appearance of a broad peak.

By contrast, low q spectra from temperature-sensitive poly(*N*-isopropylacrylamide) (NIPAAM) gels can exhibit power law behavior characteristic of fractals [36]. Koizumi et al. [36] examined NIPAAM gels over a wide temperature range and found that swollen gels, at temperatures between 28 and 34 °C, have no distinct features in the low q spectra, while collapsed gels, at temperatures between 34.5 and 36 °C, have two distinct power law regimes. The exponent in the first regime was found to be between −1.16 and −1.74, depending on temperature, and the exponent in the second regime was found to be −3.6 to −3.9. The authors interpret this as a crossover from mass fractal scattering to surface scattering, with the transition occurring at a domain size of roughly 240 nm [36].

3.3. Block copolymers and surfactants

Other than the experiments on PS–PAA micelles mentioned above [24,25], there are relatively few published USAS studies on block copolymers and surfactant systems. USANS or USAXS can provide information on very large self-assembled structures, such as rod-like micelles and giant vesicles, often complementing information from light scattering and TEM. Won et al. [37•] utilized SANS and USANS to probe the structure of aqueous solutions of poly(ethylene oxide)–poly(butadiene) copolymers (PEO–

PB), which formed either spherical or worm-like micelles. The focus of this work was to obtain detailed measurements of the segment density distribution in the PEO brushes; thus, much of the discussion focuses on meticulous modeling of the SANS data. However, by numerically fitting their combined USANS/SANS data to the theoretical form factor for a Kratky–Porod chain, the authors were able to estimate the persistence length and micelle length as 570 nm and 8.8 μm, respectively. USAS data on surfactant solutions is just beginning to appear; the best example to data is that of Hainbuchner et al. [38], who performed USANS on liposomes containing either tocopheryl acetate or vitamin A acetate. A Guinier-type analysis yielded liposome radii of 150–200 nm.

3.4. Biopolymers and biomaterials

Many biomaterials applications require structure on multiple length scales. Thus, characterization techniques that span the nano- to microscales are crucial. Materials for tissue engineering are classic examples, where micron-sized pores are necessary for cell seeding, while the structure of the bulk material and surface at the nanometer scale may impact mechanical robustness, immune response, transport of proteins and nutrients, and cell adhesion. Pochan et al. [39••,40] were the first to apply USANS techniques to biocompatible gels comprising diblock copolypeptides. At gel-forming concentrations, the scattered intensity follows a power law at low q with an exponent of −4. Similar to the attractive glasses mentioned above, the authors interpret this as surface scattering from large objects with a smooth interface. Microscopy confirms that micron-sized water channels are present in these gels [39••,40]. The low q scattering drops off drastically for concentrations that do not form gels. We have also observed large-scale structure in biocompatible poly(lactic acid)–poly(ethylene oxide)–poly(lactic acid) gels via USAXS (Fig. 3), with low q exponents of approximately −2 for most systems [41]. These copolymers form strong gels with elastic moduli>10 kPa, making them excellent candidates for engineering of cartilage and other soft tissues [42].

3.5. Other materials: colloidal crystals, composites, and nanotubes

Although a detailed discussion is beyond the scope of this review, readers interested in colloidal materials may wish to consult the series of papers by Matsuoka et al. on USAS on colloidal crystals [43–47]. Readers with interests in fractal gels are also referred to papers by Schaefer et al. on reinforcing silica and carbon [48,49] and carbon nanotubes [50••], work by Gaboriaud et al. on silica aggregates [51], experiments by Lynnard et al. on titania powders [52], and work by Livet et al. [53••] on carbon black-elastomer composites. Many of these systems have some fractal nature and exhibit scattering with some similarities to fractal colloidal gels.

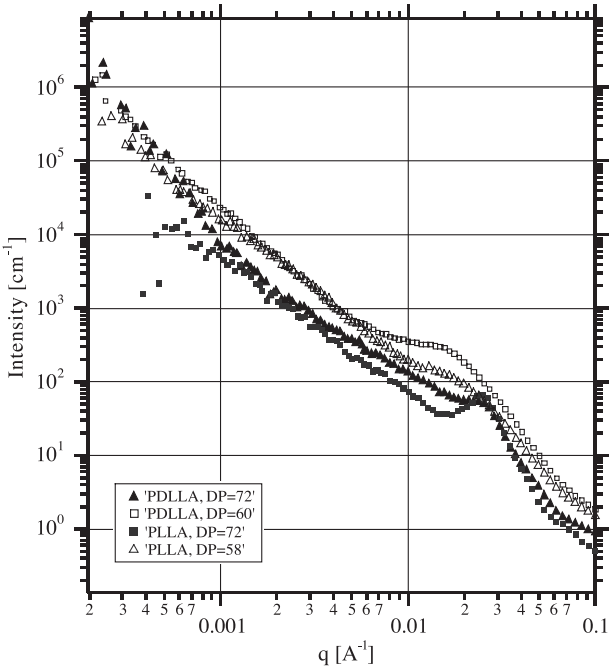

Fig. 3. USAXS spectra on a series of poly(lactic acid)–poly(ethylene oxide)–poly(lactic acid) triblock copolymers (PLA–PEO–PLA). Copolymers have the same PEO midblock length and varying total degrees of polymerization (DP) of the PLA blocks, with PLA blocks based on either D,L-lactide (PDLLA–PEO–PDLLA) or L-lactide (PLLA–PEO–PLLA). All samples show large-scale structure with a low q slope of about −2.

4. Summary and future directions

USAS techniques are clearly an important means of characterizing the assembly and structure of complex fluids and gels with multiple length scales. Often, the spectra exhibit power law behavior, yielding either the fractal dimension in the case of a networked percolated structure (with exponents from −1 to −3) or surface scattering from large dense domains (with exponents from −3 to −4). In the latter case, the spectra can often be analyzed using the models mentioned above to determine the average domain size. It is important to note that power law behavior can also be obtained for nonfractal domains that are extremely polydisperse. For some systems, a broad peak can be observed in the low q regime [17••,29••,33•], indicating a more well-defined large-scale structure with a distinct characteristic size.

In terms of future directions, USAS appears to be a promising technique for examining disordered states in soft matter (e.g., glasses and gels), where one of the important unanswered questions is the effect of the strength and range of attraction on the state and large-scale structure of attractive colloids. Low q scattering is one of the best means of determining the structure of these materials and

distinguishing between glasses and gels. The work of Lee et al. [29••] demonstrates that polymer blends with no features in conventional SANS spectra may exhibit interesting microscale morphologies revealed in the USAS range; thus, USAS may be used to uncover new morphological transitions in polymer blends and surfactant solutions. In addition, the work of Livet et al. [53••], which describes the development of a USAXS instrument with an area detector, opens up possibilities for examining anisotropic samples or samples under shear. Finally, USAS techniques are ideally suited to probe biomaterials with hierarchical structures. Although Pochan et al. [39••,40] have begun work in this area, one could easily imagine applying these techniques to microporous scaffolds and even native tissues, which to date have only been characterized using microscopy.

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