X-ray phase-contrast imaging of dynamics of complex fluids

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Abstract

Complex fluids often exhibit unusual and/or unexpected behaviours in response to external stresses because of their complicated structures and compositions. It is not easy to understand dynamic behaviours of complex fluids based on using conventional imaging methods such as optical or electron microscopy. Recently, x-ray phase-contrast imaging, as one of the most powerful methods, has been introduced for elucidating the dynamic nature of complex fluids, enabling directly looking into the insides of complex fluids thanks to the strong penetration capability and small refractivity of hard x-rays. In this paper, we review representative x-ray imaging studies on dynamics of various complex fluid systems from droplets, bubbles, granular materials and foams to colloids. It is demonstrated that x-ray phase-contrast imaging would help us better identify and utilize the properties of complex fluids.

(Some figures may appear in colour only in the online journal)

1. Introduction

Fluid is defined as a kind of substance that can flow or deform by external stress. Generally, liquid and gas are considered as fluid. Particularly, the fluids that are made of a mixture of two or more phases (regardless of solid, liquid and gas) are called complex fluids. They are ubiquitous in life, for example milk mainly composed of water-based liquid and butterfat globules, coffee of water and coffee beans, shaving cream of soap and gas and even soil of gas and sand particles. Different from pure fluids, the behaviours of complex fluids are not simply described by Newton’s law of viscosity [1–3] and are often unusual, unexpected and very interesting. For this reason, complex fluids have long attracted many scientists in the fields of physics and engineering.

One of the challenging issues of fluids is direct visualization of their complicated structures or dynamic flow behaviours. The visualization of fluids has been relying on the naked eye or optical microscopy for a long time. However, it has not been easy to acquire exact or sufficient information on dynamic behaviours of fluids with conventional visible-light imaging techniques because of several critical problems, such as (i) high scattering including reflection and refraction of the visible lights, (ii) a short depth of focus of optical lens and (iii) limitation of the spatial resolution (∼1 µm) arising from the long wavelengths (400 nm < λ < 700 nm) of the visible lights. Scanning electron microscopy (SEM) or transmission electron microscopy (TEM), which is mostly used for material science, provides extraordinary spatial resolutions to nanometre scale but is limited to surface or very small depth (∼tens of micrometres) information. Moreover, the incompatibility of liquid with vacuum environment is still the critical problem that significantly restricts the sample conditions or spatial resolutions in electron microscopy despite great improvements made by recent studies [4]. Confocal laser microscopy (CLM), using a pinhole to eliminate out-of-focus light in specimens, has come to the attention of the researchers of complex fluids and biologists due to the excellent spatial resolution...
In recent years, x-ray imaging has emerged as a new tool for studying dynamics of complex fluids. It allows in situ direct visualization and quantitative analysis in high spatial and temporal resolutions with no conditional restrictions in space, temperature and pressure. Thanks to the small wavelengths (∼100 nm) and availability of three-dimensional (3D) imaging [5]. Despite a great contribution in study for complex fluids physics, in particular, for colloid science [6–10], the confocal microscopy still has a few problems such as insufficient temporal resolution, weak penetration power to reveal the internal structure of material and the usage of fluorescent dyes.

In recent years, x-ray imaging has emerged as a new tool for studying dynamics of complex fluids. It allows in situ direct visualization and quantitative analysis in high spatial and temporal resolutions with no conditional restrictions in space, temperature and pressure. Thanks to the small wavelengths of hard x-rays (∼0.1 nm); x-ray imaging is very useful for direct visualization of small objects in thick opaque media [11].

In this paper, we review recent representative applications of x-ray imaging on dynamics of various complex fluids systems from drops, bubbles, jets, granular materials and foams to nanoscale colloids. We also briefly discuss some challenging topics that are attainable by x-ray imaging.

### 2. Complex fluids

Generally, complex fluids refer to mixtures of two phases, as shown in figure 1, such as sols (colloids) and suspensions as liquid (l)–solid (s) mixtures (figure 1(a)), bubbles and foam as g–l mixtures (figure 1(c)), droplets and jets (sprays) as g–l mixtures (figure 1(d)), granular materials as g–s mixtures (figure 1(e)) and mud or wet granulates as g–s–l mixtures (figure 1(f)). They are often called soft materials or soft matter because they are soft, specifically exhibiting viscoelastic behaviours in response to external stresses. The familiar examples of complex fluids include adhesives, paints, lubricants, slurries, biological fluids (blood, cells, etc), cement, dairy products (cheese, butter, yogurt, cream, foam, etc), sands, muds, food stuffs (sauces, chocolates, soups, cake, salad dressings, etc), inks and so on [2].

Newton’s law of viscosity that describes the flow of fluids for a fluid under a shear stress is generated perpendicular to the shear direction. The linear proportional constant is denoted as dynamic viscosity of the fluid. However, the law of viscosity is applied only to Newtonian fluids, the fluids with very limited conditions [1]. It is less than a century since complex fluids were recognized as non-Newtonian fluids of which the behaviours cannot be described by Newton’s law [2]. Complex fluids show very unusual and complicated dynamic behaviours such as shear thickening/thinning [10, 12–16] and jamming transition [17–20] that are not observed for Newtonian fluids. Detailed properties of non-Newtonian fluids are not discussed in this review, but are well explained in textbooks [1–3].

Complex fluids are used everywhere in housework and industry. Their dynamic behaviours have yet to be studied despite several efforts in this field. One of the most critical problems in understanding their phenomena is lack of experimental data. To carry out experiments on complex fluids demands much stricter conditions than on solid state materials. First, their behaviours are significantly and sensitively affected by ambient conditions such as temperature and pressure. High temperature or vacuum condition is not allowed in experimental data. To carry out experiments on complex fluids demands much stricter conditions than on solid state materials. First, their behaviours are significantly and sensitively affected by ambient conditions such as temperature and pressure. High temperature or vacuum condition is not allowed in some complex fluids. Furthermore, it is not easy to observe their dynamics since many phenomena take place in 3D in micrometre or nanometre scales, and/or are very fast, mostly in sub-second time scales. X-ray imaging can be an alternative for the visualization of complex fluids.

### 3. Phase-contrast x-ray imaging

X-ray imaging based on edge-enhancement phase contrast [11, 21–29], as shown in figure 2(a), can be an ideal methodology for the study of complex fluids because it allows non-destructive, high-speed and 3D imaging in air and at room temperature for almost non-limited thicknesses of samples.
Figure 2(b) shows an example of x-ray image for air bubbles inside a liquid medium. Boundaries of air bubbles are very clearly visible due to the refractive-index edge enhancement [21–29].

### 3.1. Coherent conditions for phase-contrast imaging

The requirement for phase-contrast imaging is sufficient coherence of x-rays [22, 27]. The coherency is generally quantified by two length scales: the coherence length along the beam direction (longitudinal or time coherence length) and the coherence length perpendicular to the beam direction (transverse or lateral coherence length). The general expressions of longitudinal ($L_t$) and transverse ($L_s$) coherence lengths are given by [22, 27]

\[
L_t = \frac{\lambda}{\Delta \lambda}.
\]

\[
L_s = \frac{\lambda D}{s},
\]

where $\lambda$ is wavelength of x-rays, $D$ is the distance between the source and the sample and $s$ is the source size. The condition for longitudinal coherence is generally given as $\Delta \lambda/\lambda \ll 2$, which is easy to meet with most of x-rays even without monochromatization [27]. The condition for transverse coherence is that $L_t$ should be larger than the characteristic length scale to be resolved of the sample [22], which is available for most synchrotron x-ray sources with source size 0.1–0.2 mm [27]. It is difficult to observe clear phase-contrast effect with low-brilliance x-ray source, such as typical lab-based x-ray source, without collimation of x-ray beam or Talbot interferometry [30].

### 3.2. X-ray microscopy

Figure 2(c) shows a typical design of in-line phase-contrast microscopy. The experimental setup includes x-ray source, optics, sample stage of complex fluids and detector system. For highly brilliant and bright beam, synchrotron is often used as x-ray source. Optic systems such as monochromator, K–B mirror or attenuators are installed between source and sample to adjust x-ray energy, position and flux. Slit and shutter systems can be used to control the beam size and the irradiation time. The detector system consists of scintillator crystal, mirror and camera. Scintillator crystal, which converts x-ray to visible light, should be carefully chosen to meet the experimental condition; thin and fast (short decay time) scintillators are needed for high-spatial resolution and high-speed imaging, respectively. A right-angle mirror is often used to protect the camera from x-ray irradiation. The camera is usually coupled with a high-magnification objective lens to control the field of view and spatial resolution.

### 3.3. Image analysis

In x-ray microscopy, the images are usually recorded using charge-coupled device (CCD) or CMOS camera connected to PC. Analysis of recorded images can be carried out by commercial image processing software like ImageJ. At first, strong edge enhancement of phase-contrast image allows one to extract boundaries of drops, bubbles or colloidal particles through a thresholding method from greyscale images. In addition, x-ray absorption can be simply measured based on pixel intensity inside each phase, enabling one to estimate the density, thickness and composition of complex fluids. Reconstruction of 3D image can be performed by commercial software such as Octopus (in CT) using multiple images taken at different angles in x-ray tomography.

For dynamic studies of complex fluids systems, various types of x-ray imaging methods have been recently tried, including tomography, ultrafast imaging, fast tomography, transmission x-ray microscopy (TXM) and so on. In the next section, experimental details and practical applications of x-ray imaging on various kinds of complex fluids are briefly introduced.

### 4. Recent applications of x-ray imaging to complex fluids

#### 4.1. Drops and bubbles: ultrafast x-ray imaging

Drops and bubbles are small masses of liquid and gas, respectively, bound by other phases or materials. We easily see many liquid drops and air bubbles in our daily lives. In particular, liquid jets or sprays composed of many tiny liquid droplets are very important in industry. Different from typical fluid flow, surface tension plays a very important role in the behaviours of drops and bubbles. First, they prefer to maintain spherical shapes as a result of surface energy minimization. For that reason, they easily coalesce into one mass when two or more drops (bubbles) get together. Meanwhile, we can see that a long column of liquid (gas) can break up into several drops (bubbles) and form liquid (bubble) jets. The coalescence and the breakup are very important singularity problems in fluid dynamics. Because their dynamics are extremely fast (∼microseconds scale) and complex, many questions still remain unsolved.

Ultrafast x-ray imaging has made a great contribution in this field. The technique requires intense polychromatic (white) x-rays, fast scintillator with short decay time, such as YAG or LYSO:Ce [31] and high-speed camera. A fast shutter is often needed to regulate the exposure time because intense white-beam x-ray can damage the sample and experimental instruments. Recently, Fezzaa and Wang [32] developed a ultrafast x-ray imaging with 3.68 μs time resolution by synchronizing beam pulse (472 ns long) from the advanced photon source (APS) storage ring with recording rate of camera. In this section, we describe four examples of drop and bubble studies using ultrafast x-ray imaging: (1) drop coalescence, (2) drop impact, (3) bubble bursting and coalescence and (4) jet and sprays.

#### 4.1.1. Singularity at the early stage coalescence of liquid drops

When two liquid drops are brought into contact, surface tension drives them to coalesce rapidly into one bigger drop (figure 3(a)). Such coalescence is a kind of free-surface...
flow phenomenon that is fundamentally important in fluid dynamics [33, 34]. One of the major issues lying on the coalescence dynamics is to elucidate how the initial contact happens, specifically whether the contact happens at a point or with a finite radius. The determination of the initial contact radius between a couple of drops at early stage of coalescence is very important to find the exponents of any scaling laws in time and the contact radius [35]. However, visualization of detailed profiles of droplet interfaces and meniscus has been challenged in visible-light imaging because of refraction, reflection or any scattering problems, as shown in figure 3(a) [34].

Fezzaa and Wang [32] successfully visualized the early dynamics of drop coalescence by developing an ultrafast x-ray full-field phase-contrast imaging technique. Through synchronization of the time structure of storage ring to the camera, they could capture one image with one x-ray pulse of 472 ns per every 3.6 µs time interval [32]. To capture the coalescence instant, electronic signals from drops were used. The time-series images of early coalescence shown in figure 3(b) make it possible to measure the meniscus radius and other features in a microsecond time resolution [32]. Specifically, the profile of drop interfaces and complex internal structure of meniscus between drops are clearly resolved. With this result, the authors concluded that the coalescence happens with a finite initial contact radius but still follows the well-known power-law scaling of \( R \sim t^{1/2} \), where \( R \) is the contact radius and \( t \) is the time [34, 35]. They also found that a toroidal bubble is really formed during the early stage [32], which had been suggested theoretically [36] but not confirmed experimentally. In this study, it was first shown that the ultrafast x-ray imaging can be an invaluable tool to study many kinds of finite-time singularities in hydrodynamics that had been difficult to access with conventional visible-light imaging methods.

4.1.2. Evolution of air during drop impact. Drop impact is another famous free-surface phenomenon. Drop impact is important because of not only fundamental interests involved but also many applications in technology such as ink-jet printing, spray coating and surface cooling. When a liquid drop hits a solid or liquid surface, it may splash, spread, breakup or bounce off the surfaces depending on the liquid drop and surface properties [38, 39]. Interestingly, ambient air that had been neglected before was found to be a new critical factor in making splash [40]. The consecutive theoretical and experimental [41–47] studies have found that a thin air film is entrapped under the falling drop (see the illustration in figure 4(a)), significantly affecting the impact dynamics. Indeed, an air bubble evolved from the air film has been observed in several studies [48–50]. However, the evolution dynamics of an air film to a bubble has remained a puzzle until recently.
Lee et al. [51] used ultrafast x-ray imaging for the first time to visualize the evolution of air during drop impact. As shown in figure 4(b) [51], the high penetration capability and phase contrast of x-rays enable resolving the detailed interface profile and complicated behavior of the entrapped air in high time and spatial resolutions. They identified three stages of evolution: inertial retraction, contraction of the top air surface into a bubble and pinch-off of a daughter droplet inside the bubble. They found that a convergence of capillary waves during the retraction of the air film drives the contraction of the air film to a toroidal shape and the pinch-off of the daughter droplet, which had been suggested by Thoroddsen et al. [50] but not confirmed experimentally. The authors also found that thedaughter droplet plays an important role to determine whether the resultant bubble detaches from or attaches at the surface. If a daughter droplet is not formed, the bubble can be detached from the solid surface only in the case of perfect wetting. Otherwise, the bubble can be detached whenever the contact angle of the daughter droplet is less than a critical value, $\sim -40^\circ$ in the case of water [51]. This study made a great contribution on the drop impact physics and on controlling of undesirable bubble-induced defects in industrial applications.

Splash study has been also realized by ultrafast x-ray imaging recently. Zhang et al. [52] visualized the formation of jets during a liquid drop impact on a bath of the same liquid. In particular, they gave for the first time the direct evidence that there are two distinct jets of ejecta and lamella, which had been suggested to exist [53] but not clearly confirmed experimentally before. They found a simple power-law scaling between the position, speed and time of the ejecta as a function of impact speed and liquid viscosity. This study shows that x-ray imaging would be useful to solve many puzzles lying under splash dynamics that are not understood today.

### 4.1.3. Bubble bursting and coalescence.

When a bubble under water rises to a surface, it bursts out with several small droplets (aerosols) jetted into the atmosphere (see figure 5(a)). This phenomenon has attracted many scientists for half a century since it plays a very important role in aerosol production, cloud formation and biological processes [54–58]. Many experimental studies have been focused on the bursting of relatively large bubbles, $\sim 1$ mm in diameter [54, 58]. In contrast, there have been few experimental efforts to understand the bursting mechanism of relatively small bubbles ($<100 \mu$m in diameter), which are entrained under the sea in great number [59]. Because the dynamics at the jetting moment is extremely fast and complicated, it is difficult to track the bubble interfaces with visible-light imaging.

The detailed evolution of a bubble bursting at the free surface was clearly visualized for small bubbles ($<100 \mu$m in diameter) by adopting a drop impact experiment using ultrafast x-ray imaging [60], as shown in figure 5(b). Using an air bubble entrapped under impacting drop [35], a bubble bursting was successfully captured at a desired time and position [60]. The formation of liquid jets during bubble bursting was found to be critically suppressed by bubble size [60]. The x-ray images in figure 5(b) show that the capillary waves travel from rupture position to the bottom of the bubble, as marked by blue points [60]. For a bubble larger than a critical size, sufficient momentum converges at the bottom of the bubble, making a jet upward. On the other hand, for a bubble smaller than the critical size, the capillary wave is strongly dampened by the liquid viscosity and the jet cannot be formed, as shown in figure 5(b) [60]. This mechanism is similar to the partial coalescence of liquid droplets [61, 62] in terms of a pinch-off of daughter droplets. In fact, the bubble bursting can be considered as a coalescence of bubbles with a finite and an infinite size. The critical Ohnesorge number ($Oh$), a dimensionless constant indicating the ratio of viscous forces to inertial and surface tension forces, was found to be $\sim 0.052$ for jetting during bubble bursting [60], which is twice that in drop coalescence [61, 62]. Using both the x-ray imaging and visible-light imaging, a phase diagram for jetting in bubble bursting was finally obtained [60]. This study would be helpful to control the aerosol production in industry [57] and to improve climate models [58].

Coalescence between air bubbles has also been studied using phase-contrast x-ray imaging [63]. Weon and Je investigated the coalescence preference that indicates the position of a resultant bubble when two or more bubbles with different sizes make contact and merge (figures 6(a) and (b)) [63]. They used an image-subtraction method to obtain the accurate positions of bubbles (figure 6(c)) and found a simple power-law relationship between positions of smaller bubble (S), larger bubble (L) and the resultant bubble (R): $a_S/a_L \sim (r_L/r_S)^{-5}$ [63], where $a_L$ and $a_S$ are the distances between the larger and smaller bubble from the centre of the resultant bubble, and $r_L$ and $r_S$ are the radius of the larger and smaller bubble, respectively. The exponent $-5$ is different from that of the centre-of-mass theory, $-3$, but similar to that...
of surface energy release theory $−5.3$ [63], demonstrating direct evidence that the coalescence preference is determined by surface energy release rather than the centre of mass theory. This result shows another example that x-ray imaging can be a useful tool for coalescence physics of drops and bubbles.

4.1.4. Liquid jets and sprays. One of the most frequently used complex fluid systems in industry is liquid jets or sprays, but the understanding of the breakup or atomization mechanism of jets has been quite poor for a long time. Especially for a dense liquid jet, the flow visualization based on visible-light imaging has been limited by absorption, reflection and multiple scattering by complex morphology and a large number of droplets. To solve this problem, several efforts using x-ray imaging have been made recently. The first use of x-ray imaging with phase retrieval reconstruction [64] has successfully obtained 3D information of water volume fraction, but failed to measure the flow of the jet. Another attempt of x-ray particle tracking velocimetry enabled velocity mapping of a pipe flow [65]. Tracking particles is frequently used in flow visualization but is still an invasive method because buoyancy, particle interactions and shapes can affect the flow properties.

Using ultrafast x-ray phase-contrast imaging, Wang et al [66] developed structure-tracking velocimetry for the first time to measure the time-dependent morphology and velocity fields of high-speed dense liquid jets. The x-ray images obtained by double-exposure method (with 472 ns exposure time and 3.68 $\mu$s delay) are shown in figure 7(a) [66] and the intensity autocorrelation functions of the corresponding regions marked as boxes in figure 7(a) are shown in figure 7(b) [66]. For all three images shown in figure 7(b), a bright central peak corresponds to the self-correlation of the x-ray image and pairs of symmetric peaks correspond to the correlation of the two double-exposure x-ray images. The instantaneous velocities can be calculated by the basis of peak positions in the autocorrelation functions, as indicated by arrows in figure 7(b) [66]. The main contribution of this work is that the authors successfully obtained the velocity field of liquid jets without the help of tracer particles.

Further efforts using x-ray imaging have been devoted to solving some important issues related to liquid jets. For example, Wang et al [67] reported strong evidence that the atomization of liquid jet follows cascade forms as proposed [68], which had been controversial for a long time [69–71]. They visualized the breakup dynamics with different air speeds.
by multiple-exposure methods, as shown in figure 7(c) and demonstrated that the cascade breakup processes occur in very similar fashions due to capillary instabilities [67]. The ligament-type breakups with relatively lower air speed are clearly visible in the ‘a’ and ‘b’ images of figure 7(c), while the membrane-type breakup with relatively higher air speed is clearly visible in the ‘c’ image of figure 7(c) [67].

The other examples are about the shock wave generated by liquid jets. An unusual ambient gas distribution around the shock was clearly visualized by time-resolved x-ray radiograph [72] and this was found to be the results of the aerodynamic interaction between the liquid jet and the shock waves based on using high-speed x-ray radiography [73].

4.2. Granular materials: fast radiography and x-ray tomodraphy

Granular materials that are large conglomerations of discrete solid particles are also a kind of complex fluids with solid particles as solute and gas as solvent. There are numerous types of granular materials used in our present life and industry, such as sand, nuts, wheat, sugar, beans, rice, coffee, fertilizer, asphalt, lime powder and ball bearings. Their properties and behaviours are much different from those of typical phases such as gas, liquid and solid. Some argue that granular materials have to be considered as a new additional state of matter [74]. Despite their prevalence and importance, most of the phenomena related with granular materials have not been well understood and explored due to lack of constitutive equations describing the whole phenomenology of granular flow [75]. Thus, granular materials have been one of the hottest issues in the complex fluid field recently.

X-ray tomodraphy and radiography have been very recently applied to the study of granular materials. The tomodraphy technique is a very useful tool to reveal 3D structure of materials. The experimental setup is similar to that shown in figure 2(c). The sample is located on the mechanical rotary stage and rotated for 180° in multiple steps for one set of 3D data. The images are taken at different angles with typically 100–1000 frames and collected to reconstruct a 3D image. In this section, we will briefly introduce several reports on new important aspects of granular materials physics, revealed by x-ray imaging.

4.2.1. Granular jets revealed by ultrafast x-ray imaging.

Similar to drop impact [76], an upward jet composed of sand particles is formed when a heavy sphere impacts a bed of loose and fine-grained sand [77–79]. However, the underlying physics is totally different. While the jet formation in drop impact mainly results from the surface tension of liquid [76], the granular jet does not require any surface tension and cohesion. Early works [77, 78] proposed that a crater created by the impact of a heavy sphere collapses abruptly by gravity, generating a pressure spike, which promotes the formation of a strong granular jet. However, the experimental evidence supporting the model has been poor because of the lack of adequate imaging methods.

Royer et al [80] used x-ray imaging to observe the jet formation inside the granular bed and demonstrated that in fact the jet formation is created through more complex process than assumed. The high-speed x-ray imaging revealed the morphological evolution in 3D during the impact of a sphere, as shown in figure 8 [80]. They found that the abrupt pinch-off of the cavity promotes concentration of momentum at the central axial region, making a thin jet strongly raised upward [80]. Moreover, an air pocket is trapped by the pinch-off, driving a formation of thick secondary jets under a sufficient ambient air pressure. The main contribution of this work is that the ambient air, a new parameter, plays an important role in granular jet formation.

4.2.2. The unusual stability of wet granulates revealed by x-ray tomodaphy.

You may remember that a sand castle at the beach becomes solid when a small amount of water is added. The reason for the remarkable stability of such wet granulates is that the surface tension of water provides considerable stiffness to the material by forming bridge structures between the adjacent solid particles [81, 82]. Interestingly, mechanical properties are almost invariant whatever amount of liquid is added [83]. The invariance has been well understood for small liquid contents because the increase in the liquid bridge size with liquid volume is balanced with the decrease of the bridge curvature [81]. However, understanding of mechanical properties for large liquid contents has been poor because of significant changes in internal liquid morphologies such as coalescence of liquid bridges and formation of cluster structure [82, 84, 85].
The underlying physics for stability of wet granulates has been elucidated by Scheel et al [86] using x-ray tomography technique. The x-ray slice images of internal structure of wet granular pile at different liquid contents are shown in figure 9(a). The quantitative parameters such as average number of liquid bridges on a single particle, average number of clusters per particle and volume of the clusters were measured from the images [86]. Using the ratio between the surface area and the volume of each cluster, the authors identified the clusters as dimer (capillary bridge, cb), trimer (tr), pentamer (pt) and filled tetrahedra (th) obtained from x-ray tomography. Bottom row: numerically obtained cluster structures corresponding to that of top row. (c) Illustration of capillary bridge structure between two spheres [86]. R is the radius of a sphere, β is the bridge angle and θ is the contact angle of bridge. Reprinted with permission from [86]. Copyright 2008 Nature Publishing Group.

4.2.3. Investigating packing of granular materials by x-ray tomography. Packing of grains is an old issue in statistical physics. X-ray tomography has also been used for investigating such packing. For example, Richard et al [88] studied the evolution of packing structure of beads that are compacting under vertical vibration and showed that the volume distribution of pores exhibits a broad exponential tail, which consistently reduces upon the compaction. Zou et al [89] also used x-ray tomography to investigate the packing of chains connecting hard spheres and found that long chains pack into a low-density structure consisting of randomly oriented semi-rigid loops that formed during the compaction of chains. This study provided an important analogy between the packing of chains and the glass transition in polymers. These examples show that x-ray tomography can be an invaluable tool to understand physics of packing in various systems.

4.3. Foam: 3D coarsening explored by x-ray tomography

Foam is another type of complex fluid composed of many bubbles bound by liquid. Many types of foam are easily seen in our life, for examples, soap foam, shaving foam and coffee foam. Foam has been intensively studied for a long time because it is a good model to understand the coarsening of diphasic system. Coarsening, sometimes called Ostwald ripening, describes the slow change of internal structure of diphasic materials by diffusion driven by interfacial energy. The variation of curvatures between adjacent domains make capillary pressure gradient, promoting the diffusion from a smaller to a larger domains through the continuous phase to reduce total surface area. Over time, the smaller domain gets smaller and is eventually consumed by the larger one. This results in the decrease of a total number of domains and the increase in average size of domains, finally simplifying the internal morphology of materials.

Coarsening dynamics in two-dimensional (2D) systems has been well understood. According to von Neumann’s law [90], the growth rate of each domain does not depend on its size and shape but on the number of sides (n). Interestingly, the growth rate of average sizes (G) of domains follows a simple power law: \( G \sim t^{2/3} \) [91]. In addition, the normalized statistic distributions of domain sizes and topologies (n) show remarkable self-similarity over time [92]. However, coarsening in 3D is not so simple as 2D. The domain growth in 3D is not simply proportional to the number of neighbours [93]. Several theoretical models for coarsening in 3D were postulated [93–95] with few experimental studies to support the models until recently. 3D visualization is difficult because thin liquid films and Plateau borders in dry foam strongly scatter the visible light. Some 3D imaging methods such as magnetic resonance imaging [96] and optical tomography [97] still have limitations in spatial and temporal resolutions and in statistical reliability.

4.3.1. Foam growth revealed by x-ray tomography. To uncover the physics of 3D coarsening of liquid foam, x-ray tomography has been tried recently. In fact, it had been difficult to apply x-ray tomography to dynamic study because
found that the average bubble size increases as the square root of time after a transient regime. Furthermore, the statistical distributions of the bubble size and the face number showed scale invariance [100], as in 2D foam growth [92]. These works have far improved understanding of 3D coarsening.

4.3.2. Fast tomography. Recently, x-ray tomography has been further upgraded in timescale, resulting in real-time, fast tomography [101]. Such fast tomography requires (i) the increase in the photon flux by using bright x-ray source such as polychromatic beam, (ii) the use of a high-speed camera with a big internal memory to dramatically reduce the readout time and (iii) continuous rotation of the sample with high speed synchronized with the camera. The acquisition time can be reduced in this technique to sub-second by the performances of current rotary stages and high-speed cameras. Mokso et al [102] reduced the acquisition time to 0.5 s using quasi-monochromatic x-ray as a source and showed that the early stage of foam growth could be imaged without addition of any stabilizer agent like C6F14, used in previous studies [99, 100]. More recently, Jung et al [103] used bright monochromatic beam with highly optimized optic systems and visualized the rising bubbles with only 0.25 s exposure time, as shown in figure 10(c). The use of a monochromatic beam for such a fast microtomography would be a great advantage in studying foam, taking into account possible evaporation of liquids by high-flux x-ray [104].

4.4. Colloids: dynamics of colloidal particles visualized by TXM

Colloids, composed of dispersed small particles (10 nm–1 μm in size of solid, liquid or gas) and continuous medium, are representative complex fluids system and have been widely studied for a long time. The detailed properties of colloids are well summarized in [9, 105]. Their small sizes make it difficult to observe them with optical microscopy. Instead, CLM has been mainly used to observe and characterize colloidal behaviours. Although CLM has shown excellent performance in colloid science [6–10], it is still limited to studying refractive-index matched particles dyed with fluorescent materials. Its spatial resolution (~100 nm) is not sufficient to allow detailed quantitative study either.

Recently, x-ray imaging came into use to reveal the internal structure of colloid structures. A variety of optical techniques have been coupled to x-ray imaging to enhance the spatial resolution [106]. Here, we review representative results of colloidal systems achieved by Fresnel lens-based x-ray imaging, so-called TXM. The layout of TXM is schematically shown in figure 11(a). It consists of a capillary condenser, a pinhole, a sample stage, a Fresnel zone plate, a phase ring and a detector system. Monochromatic x-rays are focused on the sample position by the capillary condenser. The pinhole is installed to eliminate unwanted illumination to enhance the imaging quality. The Fresnel zone plate objective, a key element determining performance of TXM, is installed behind the sample to diffract the x-ray beam. For imaging of low-absorbance materials, the phase ring is inserted to
enhance the phase shift effect. The detector system includes scintillator and high-sensitive CCD. In recent years, it has been reported that the spatial resolutions (Rayleigh resolution) of both the absorption imaging and phase-contrast imaging reach a $\sim 30$ nm level [107–109].

4.4.1. X-ray induced sintering of PMMA colloidal particles.
One interesting application of TXM to colloid system is x-rays-induced sintering of colloidal particles [110]. The sintering or coalescence of colloidal particles is an important process for constructing novel architectures such as photonic crystals. The sintering of conventional ceramic materials requires high heat and pressure, which is not adequate for polymer colloid materials because of thermal damage. Weon et al [110] reported a new x-ray-induced sintering without using any heat and/or pressure. Under irradiation of focused synchrotron monochromatic x-rays, the PMMA colloidal particles coalesce into a single mass, as clearly shown in figure 11(b) [110]. The x-ray irradiation is explained to induce the photochemical scission of colloids, reducing the molecular weights. This results in the decreases of the glass transition temperature, the surface tension and the viscosity of PMMA. This work proposed a new protocol for room temperature sintering of PMMA colloid particles, which can be applied for nanofabrication of soft materials [111].

4.4.2. Wettability of colloidal particles. Another example is the investigation of colloidal wettability at an interface [112]. Colloidal particles can spontaneously accumulate at an interface between two immiscible fluids such as oil/gas or water/oil. This is a driving force of famous Pickering emulsion [113]. The microscopic wetting state of colloidal particle at the interface has been recently revealed by TXM. Weon et al [112] used both the TXM and CLM to visualize accumulated particles and a single particle dyed with fluorescent at an interface, respectively. They showed that the wetting angles can be measured consistently in both systems, demonstrating x-ray imaging as a promising tool in colloid research.

4.4.3. Internal structure of colloidal photonic crystals. The excellent performances of TXM also enabled to explore internal structure of colloidal photonic crystals. Bosak et al [114] firstly reported the application of phase-contrast TXM to photonic crystals using hard x-rays (12 keV). Schooneveld et al [115] and Hilhorst et al [116] used scanning type of TXM using soft x-rays based on absorption contrast to visualize the colloidal structures. The local structure such as positions, orientations, deformations and even defects such as vacancies and stacking faults of the colloidal structures were successfully revealed by high performance of TXM [115, 116].

5. Perspectives: challenging subjects in complex fluids

5.1. Liquid drop impact onto liquid surface
There are many interesting problems related to drop impact on liquid surfaces. For example, liquid drop falling into a liquid bath generally entraps a small bubble underneath [117, 118]. This bubble entrapment, which can be easily seen in the breaking waves, is a very important process to transport the gas to seawater. Such bubbles burst at interface and generate aerosols, as discussed in section 4.1.3. When an impacting speed is relatively slow, a vortex ring enclosing the drop is observed [119, 120]. In contrast, when the impacting speed is relatively fast, a vortex street can be formed at the bottom surface, as simulated by Thoraval et al [121]. In this case, a splash occurs at the top of liquid surface, which is an old problem in drop impact [38, 39].

Most of these phenomena are still far from being fully understood. The common characteristic is that they occur through a very complex morphological evolution in thick liquid medium. This makes it difficult to visualize them with conventional optical imaging. The ultrafast x-ray imaging would be very useful to figure out the underlying physics of those phenomena.
5.2. 3D coarsening law

Recently, the most advanced model for 3D coarsening has been formalized [95]. The model explains that the grain growth rate depends on 1-D parameters of grain: the linear size and sum of the edge lengths. The model has a very simple form, compared to previous models (for example, [94]), and is quite similar to that in 2D coarsening. The statistical features of self-similarity in 3D coarsening of liquid foam with a large number of bubbles have been revealed by x-ray tomography [99, 100], as discussed in the section 4.3. However, the experimental verification of the 3D coarsening model [95] is still lacking. It would be a great breakthrough if an exact 3D coarsening model could be found by fast x-ray tomography.

5.3. Wetting at nanoscale

Classical wetting of liquid droplet on hard surface is often explained by Young’s law [122]. In this case, the wetting angle θ is given as \( \theta = \cos^{-1}\left(\gamma_{SV} - \gamma_{SL}/\gamma_{LV}\right) \), where \( \gamma \) is the interfacial tension between two states of solid (S), liquid (L) and vapour (V). In contrast, the wetting angle of liquid droplet on immiscible liquid surface, i.e. perfectly soft surface, is determined as \( \sin \theta = \gamma_{SV}/\gamma_{SL} = \sin \theta_v = \theta_{SV}/\theta_{LV} \) (S denotes surface in this case), which is known as Neumann’s law [121]. Generally, the wetting angles between two cases are totally different. Then, what will be the wetting angle of liquid droplet on intermediate surface, i.e. viscoelastic surface? Several theoretical models were proposed but still far from the exact answer [123, 124].

The wetting angle on soft solid surface has been investigated by experiments only recently. Fluorescent confocal microscopy was used to reveal the profile of surface deformation and demonstrated that soft surface exhibits a cusp at the contact line [125]. However, fluorescent dyes used in confocal microscopy may affect the interfacial tensions between phases and change the wetting angle. A non-invasive, direct visualization method with submicrometre resolution is required. We believe that TXM could be an alternative to study the very small deformation of soft surface and reveal the secret of wetting.

6. Conclusions

The field of complex fluids is rapidly growing up now because of the fundamental interest and its importance in various industrial applications. Of course, synchrotron x-ray imaging is not a very common tool in studying complex fluids, but has made great contributions to elucidating many important phenomena in complex fluids, as discussed in this review. The extraordinary performances of x-ray imaging in a variety of applications demonstrate enormous possibilities in investigating complex fluids. X-ray imaging methodology is still under development by many scientists. Further improvements in x-ray imaging may open greater opportunities for scientists to much better understand the underlying physics of various phenomena related to complex fluids.
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