1. Introduction

A system in which a large number of gas bubbles are dispersed in a continuous liquid or solid is called a foam. The gas can be air, nitrogen, carbon dioxide and so on, that coexists with the liquid vapour. While the liquids can be water (aqueous solutions), oils (organic solvents), ionic liquids or molten metals, we consider, in particular, air bubbles dispersed in aqueous media in this paper. In general, ionic or non-ionic surfactants and surface-active polymers (including proteins) are used as the stabilizing agents for foams, because they can be adsorbed at the air-water interface and thereby reduce the interfacial energy of the interface. In addition to such molecular foam stabilizers, it has been also well known for over a century that particles can act as stabilizers for foams\(^1\). There have been a relatively large number of systematic studies of particle-stabilized emulsions consisting of oil and water: oil-in-water emulsions are formed if the particles are more wetted by water than by oil (relatively hydrophilic particles), while water-in-oil emulsions are formed for relatively hydrophobic particles\(^2\). Considering that air can be considered as an oil with an extremely low polarity and density, it is not surprising that solid particles stabilize foams by adsorbing to air-water interfaces. Such foams stabilized by the particles are observed and utilized in a wide range of industrial fields such as flotation, washing, food, water treatment, treatment of radioactive wastes, and distillation in the petroleum industry, etc\(^3\). In recent years, after a dormant period of nearly half a century, there has been a resurgence of interests in the field of solid particles adsorbed at air-water interfaces. There is a large number of researches on foams using solid particles as foam stabilizers (or foam-breaking agents) in the presence of molecular surfactants\(^2b,2d,4\). In such surfactant-particle mixture
systems, as both surfactants and particles can adsorb at the air-water interface competitively and the surfactants can adsorb to the surface of particles, the mixture systems would be more complex to be analyzed than the independent systems. Therefore, it is thought to be important to carry out researches on foams stabilized solely with particles to obtain fundamental knowledge about the role of particles in foam stabilization. Moreover, sometimes it would be desirable not to add surfactants in some practical applications. Under such circumstances, recently, researches have been started on the foams solely stabilized with particles in the absence of any molecular surfactants. These particle-stabilized foams are formed by using relatively hydrophilic particles. The question arises what will happen if relatively hydrophobic particles are mixed with water (or polar liquids). The materials prepared by aeration of the relatively hydrophobic particles and water have been shown to be water drops dispersed in air (water-in-air material), represented by dry water (liquids) and water (liquid) marbles. The dry water consists of small water drops coated by the hydrophobic particles in air and behaves as a powder. This kind of water-rich powdery materials was first described in the 1960s and the inversion between aqueous foams and water-in-air materials has been realized by controlling the stabilizing particle hydrophobicity and the air-water volume ratio. This new class of methods of water (polar liquids) encapsulation in air would lead to promising applications in cosmetics, pharmaceuticals and food industry.

In this overview, we focus on the researches related to aqueous foams and liquid marbles (dry liquids) that are stabilized by particles. The particles presented in this article are inorganic particles and organic polymer particles. The inorganic particles such as silica and alumina can be commercially obtained in relatively large quantities from a number of companies and are frequently used for fundamental studies on particle-stabilized foams and liquid marbles. In addition to the inorganic particles, the organic particles have recently been used as particulate foam and liquid marble stabilizers. Due to the development of technologies to design, synthesize and characterize the particles, the organic particles with precisely controlled surface/inner structures have found their applications in various industrial and academic sections. Successful particle synthesis would inspire the construction of well-defined and functionalized particle-stabilized foams and dry liquid systems.

![Diagram of foam stabilization](image)

**Fig. 1** (a) Small spherical particles adsorbed at an air-water surface; a relatively hydrophilic particle (θ < 90°, left) and relatively hydrophobic particle (θ > 90°, right). (b) Four quadrants of dispersed systems comprising of water, oil and air stabilized by particles. In mixtures of oil and water (upper quadrants), relatively hydrophilic particles stabilize oil-in-water type emulsions, while relatively hydrophobic particles stabilize water-in-oil type emulsions. In mixtures of air and water (lower quadrants), air-in-water materials (bubble, foam) are formed by using relatively hydrophilic particles and water-in-air materials (water marbles, dry water) are formed by using relatively hydrophobic particles. (c) Whipped cream-like foams produced by aeration of water and relatively hydrophilic silica particles. (d) Dry water comprising water drops coated by hydrophobic particles in air, showing a free-flowing property. [Quoted from reference 7(a). Copyright, Nature publishing group.]
2. Particles Adsorbed at Air-Water Interfaces and Methods of Their Evaluation

2.1 Adsorption of particles at air-water interfaces

Based on the discussion regarding the effect of the particle wettability toward oil-water interface on a type of particle-stabilized emulsions\(^{2b, 20}\), it is expected that relatively hydrophilic particles (contact angle which particles make at the air-water interface measured through the water phase, \(\theta_{aw}\), is less than \(90^\circ\)) are suitable to stabilize air bubbles dispersed in water and that relatively hydrophobic particles (\(\theta_{aw} > 90^\circ\)) are suitable to stabilize water droplets dispersed in air (see Fig. 1)\(^7\). Binks et al.\(^7\) have demonstrated a phase transition between a system of air bubbles dispersed in water (foam) and that of water droplets dispersed in air (dry water: a free-flowing powder consisting of water drops coated by hydrophobic particles) by controlling the hydrophobicity of silica nanoparticles (see Fig. 1). Therefore, it is considered that even in particle-stabilized dispersed systems consisting of air and water, similar to those consisting of oil and water, the wettability of particles can be handled as one of very important factors that control the characteristics of the systems.

Assuming the particle is small enough (typically less than a few micrometers in diameter) so that the effect of gravity is negligible, the energy change when a spherical particle adsorbed at the air-water interface is removed from the interface (\(\Delta G\)) is expressed by the following equation\(^1\).

\[
\Delta G = \gamma_{aw} \pi a^2 (1 \pm \cos \theta_{aw})^2
\]

Here, \(\gamma_{aw}\) is the surface tension of the air-water interface, \(a\) is the radius of the particle and the sign inside the bracket is negative for removal into the water phase and positive for removal into the air phase. This equation indicates that \(\Delta G\) is related not only to the contact angle but also to the air-water interfacial tension: the energy of adsorption becomes large as the particle diameter and the interfacial tension increase and the contact angle is close to \(90^\circ\). Once the particles are adsorbed to the interface, it is difficult for them to desorb from the interface because of the high adsorption energy (relative to the thermal energy \(kT\)). This is in sharp contrast to surfactant molecules which adsorb and desorb on a relatively fast timescale. Hence it is expected that the stability of the foams stabilized by particles with a suitable wettability to air-water surfaces is higher compared to those stabilized with the molecular foam stabilizers.

2.2 Experimental evaluation of particles adsorbed at fluid interfaces

For many years, research has been conducted on the establishment of the method of measuring the contact angle of colloidal particles adsorbed at fluid-fluid interfaces. In the past several years, several types of new measurement methods have been proposed and have attracted attention. Paunov\(^{22}\) has proposed a method called the gel trapping technique. After adsorbing particles at an air-aqueous solution of gelatine interface at 50°C, the aqueous phase is made into a gel by lowering the temperature to room temperature, and the particles are fixed at the interface. Next, poly(dimethylsiloxane) (PDMS) was slowly poured above the gelatine having the particles fixed at the surface and then PDMS was crosslinked. Then, by pulling apart this PDMS layer from the gelatine, the particles transferred onto the surface of PDMS, and this is observed by scanning electron microscopy. Butt et al.\(^{13}\) have succeeded in measurement of the contact angle of the particles at an air-water interface using a colloidal probe atomic force microscope (AFM) (see Fig. 2). In this method, the single particle was attached to a cantilever of the AFM and a force curve obtained from the relationship between the particle and the air bubble using the cantilever was studied. It is worthy to note that the energy for the particle adsorbed at the air-water interface to desorb particles from the interface to the water phase can be also measured by using this method.

Recently, a simple and rather direct method to measure contact angles of relatively hydrophilic particles (\(\theta_{aw} < 90^\circ\)) adsorbed at an air-water interface in situ has been developed\(^{14}\). In this method, named film-calliper method (FCM), some particles adsorbed at an air-water thin film bridging both surfaces by sucking liquid out of the film meniscus are utilized (Fig. 3a). Once the particles bridge both air-water interfaces, characteristic interference patterns of dark and bright fringes are observed. The patterns are recorded using a horizontal microscope in reflected monochromatic light (Figs. 3b, 3c). By analysing the interference pattern, the film thickness profile and the film thickness at the location of the bridging particle \(h\) at a different degree of shrinking of the film achieved by pumping water into the meniscus can be plotted against the radial distance from the center of the film (Fig. 3d). The bridging particle location is independent of the film profile as any deformation of the film surface associated with the particle immigration causes an increase in surface free energy. Hence, the contact angle of the bridg-
ing particles are simply determined by an equation. 

\[ \cos \theta_{aw} = \frac{h_e}{d} \]

where \( d \) is the particle diameter. The contact angle values of micrometer-sized particles obtained by the FCM are in excellent agreement with those determined by previously developed other optical methods (side imaging and film trapping techniques). Moreover the FCM has an advantage of applicability to measurement of contact angles of particles with a diameter of submicrometer.

3. Foams Stabilized with Smart Particles

Foams stabilized with particles are observed and utilized as either intermediates or as end-products in various industrial sections, such as flotation, washing, food, water treatment, treatment of radioactive wastes, and distillation in the petroleum industry. In many other unit operations, which frequently involve mixing of gas and liquids by pumping or stirring, the presence of solid particles can lead to undesirable foaming. For example, in the paper industry, detri-
mental foams are frequently generated which are stabilized by fibre, tars, and minerals such as clays. Such foaming can cause problems by blocking pipes and filters, and it makes monitoring of flow in pipes difficult. In the oil industry, obnoxious foams are produced in boilers and at various stages of distillation which are thought to be stabilized by asphaltene particles. In other cases, insoluble precipitates (partially hydrophobic particles from washing or hydrolyzed cationic precipitates such as iron oxide from steel mills) are adsorbed at air-water interfaces and can also cause foaming in effluent discharges feeding into rivers. However, in the fields of ore flotation and deinking flotation, foams are used effectively in order to make particles adsorbed at air-liquid interfaces and to recover the target materials. The particle-stabilized bubbles are also observed in space. Vanderhoff and Shaffer reported that nitrogen bubbles were stabilized with monodisperse polystyrene (PS) particles adsorbed at a nitrogen-water interface: the nitrogen bubbles would be formed by decomposition of azo-initiator during seeded emulsion polymerization experiment aboard the space shuttle orbiter Challenger (STS 7, June 1983). In space, the bubbles show no tendency to cream; therefore, the bubbles are stable against breakage caused by liquid drainage. For emulsions, consisting of oil and water, stabilized with particles, two stabilization mechanisms have been proposed. One is the mechanism of preventing the three-dimensional coalescence between liquid droplets and the diffusion of dispersed phases (oil, water) owing to densely packed adsorbed particle layers on the interface of the liquid droplets, i.e., formation of two-dimensional solid (steric stabilization mechanism: SSM). The other mechanism is formation of a single particle layer simultaneously wetted by two liquid droplet interfaces, preventing the coalescence between the liquid droplets (bridging stabilization mechanism: BSM). In foam systems, although any examples of the BSM have not yet been reported at this stage, stabilization by the SSM has been reported. Furthermore, it has been shown that air bubbles sufficiently covered with particles own enough surface elasticity to prevent disproportionation of bubbles.

3.1 Features of foam (air bubbles) stabilized by particles

3.1.1 Stabilities against coalescence and disproportionation

Foams, which are generally formed by stirring gas and liquids or by injection of gas into liquids, are thermodynamically unstable and eventually return to the initial separated two phases due to coalescence between bubbles and diffusion of gas from smaller bubbles to larger ones (disproportionation). However, it has been reported that foams stabilized by particles exhibit high stability against both coalescence and disproportionation.

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3.1.2 Non-spherical shapes and wrinkled skins of particle-stabilized foams

While bubbles stabilized by molecular surfactants take the spherical shape in order to minimize the interfacial area between air and liquid, in the case of air bubbles stabilized by particles, the bubbles can take not only the spherical shape but also the nonspherical shapes (elliptical, rod shape, etc.). This occurs because particles with a suitable wettability are irreversibly adsorbed to the air-water interface, and it is not practically possible for particles to be detached from the interface even if the area of the air-water interface decreases when two air bubbles covered (partially) with particles coalesce with each other. The inability of the particles to be expelled from the bubble surfaces also leads to the wrinkled bubble skins.

3.2 Foams stabilized with inorganic particles

Some typical inorganic particles used as a foam stabilizer are inorganic oxides such as silica, alumina and clays, and their surface characters are generally hydrophilic. As has been shown in the research on ore floatation, the adjustment of the hydrophobicity of particles is generally performed by addition of amphiphiles (surfactants) into the aqueous phase. By selecting appropriate combination of amphiphiles and particles, the synergistic effects (enhanced foam volumes and stability) can be induced. In the amphiphile-particle mixture systems, however, both of them are adsorbed at air-water interfaces competitively, and their contribution to foam formation and stability may overlap. Therefore, it is expected that studies on foams stabilized by particles in the absence of amphiphiles enable us to obtain fundamental knowledge on the role of particles in the stabilization of foams. In this section, an outline is presented of research on foams stabilized by inorganic particles; (1) mixture systems of amphiphiles (surfactants)-inorganic particles where the wettability of particles is modified by adsorption of amphiphiles onto the particles, and (2) single systems of inorganic particles where the wettability of particles is controlled.
by changes in particle surface chemistry and pH or salt concentration in water.

### 3.2.1 Foams stabilized by mixtures of amphiphiles (surfactants) and inorganic particles

Ionic surfactants with opposite charge against particle surface charge have been used to control hydrophobicity of the particles diversely. For example, silica particles are negatively charged in aqueous dispersions at pH > 2 due to dissociation of proton from the surface silanol groups. In the presence of cationic surfactants such as alkylammonium salts, it has been known that positively charged hydrophilic groups are bound to the negatively charged surface silanol groups, with the hydrophobic groups of the surfactant orientating to bulk water phase, due to the electrostatic interaction\(^{21,22}\). The silica particle surfaces are covered by hydrophobic alkyl chains with increasing the surfactant concentration in water, and hence the hydrophobicity of the particles becomes increased. Further increase in the surfactant concentration, however, leads to the formation of bilayer of the surfactant at the silica particle surfaces, which render the silica particles back to hydrophilic\(^{21}\). The maximum foam production occurs at the intermediate surfactant concentration, where the particles are barely charged and the most hydrophobized.

Recently the group in ETH-Zurich have adjusted the wettability of inorganic particles (Al\(_2\)O\(_3\), ZrO\(_2\), Ca\(_3\)(PO\(_4\))\(_2\), SiO\(_2\)), that are charged positively or negatively in aqueous media, by mixing with amphiphiles with short hydrocarbon chains (carboxylates, amines and gallates)\(^{23}\). The amphiphilic substances adsorb and orient onto the particle surfaces with the hydrophilic groups towards the surface of the particle through the electrostatic interaction or ligand-exchange interactions, and the hydrophobicity of the particles increases with increasing the amphiphile concentration in the aqueous phase (see Fig. 5). Using a relatively large quantity of particles (35 wt % at maximum), the foams show significant stabilities against coalescence, disproportionation, and creaming.

### 3.2.2 Foams stabilized by inorganic particles alone

Among inorganic particles, silica particles are used frequently as the model particles as they are relatively easily available as high purity products. Furthermore, as reactive SiOH groups are present on the surface of silica particles, using suitable hydrophobizing agents (for example, dimethylchlorosilane: DCDMS), it is facile to adjust the hydrophobicity on the surface of particles chemically. The extent of hydrophilicity of the silica particles is quantified by the unreacted surface SiOH groups (100%SiOH: extremely hydrophilic, 20%SiOH or less: extremely hydrophobic). Binks and Horozov have shown that, the particles with a suitable hydrophilicity can form
foams that are stable with respect to coalescence and disproportionation, although hydrophilic (≥70% SiOH) and extremely hydrophobic (14% SiOH) particles can not stabilize air bubbles. The individual air bubbles obtained are not spherical in shape, and the surfaces of air bubbles are not smooth but wrinkled. In addition, from the fact that the silica particles developed at a plane air-water interface form such wrinkles at a high surface pressure, it is suggested that the air bubbles are covered with dense particle layers (see Fig. 4).

The silica particles wettability can be adjusted by controlling compositions in water. By using nanometer sized fumed silica particles, the same type of particles as described above, the effects of pH and electrolyte concentration in water on the wettability of the particles and the foam stability have been investigated. For example, aeration of relatively hydrophilic silica particles (66% SiOH) and water results in an aqueous dispersion of the particles, however when the particles are aerated with aqueous solutions of NaCl, foams are formed. The stability of the foams (referred by foam volumes after a period of preparation) increases with increasing the NaCl concentration (see Fig. 6). It has been suggested that the addition of electrolyte to the water phase induces not only shortening the Debye length, but also changing the hydration structure on the surface of the silica particles are responsible for the observed increase in the hydrophobicity of silica particles.

3.3 Foams stabilized with organic particles alone

Organic polymer particles have mainly been used in the form of film in paint and adhesive industrial sections. In addition to the usage in the form of the film, there have been increasing interests in using the polymer particles in their particulate form. The polymer particles have been used as absorbents, ion-exchangers, affinity bioseparators, drug and enzyme carriers, viscosity modifiers, support materials, calibration standards, and functional beads for medical diagnostics. The utilization of the organic polymer particles as a building block toward colloidal crystal is also attracting attention. The latex particles have also found their application as emulsion and foam stabilizers. Studies on the aqueous foams stabilized with polymer particles have recently been started, and advanced applications of these foams should be expected, considering the varieties of polymers. In aqueous dispersion of such organic particles, the particles themselves are electrostatically and/or sterically stabilized against flocculation. In this section, researchers on aqueous foams stabilized by organic polymer particles with their respective stabilization mechanisms are described.

3.3.1 Charge-stabilized organic particles

Wilson explored the foaming behavior of charge stabilized anionic PS latex particles with diameters ranging from 1.02 to 3.89 μm. Foaming could only be achieved after addition of either salt or cationic surfactant, or by making the latex highly acidic (pH < 1). Thus, the conditions required for generating stable foams either approached or exceeded those required for aggregation of the latex particles in bulk aqueous solution. Moreover, the foam quality decreased as the latex diameter was reduced, with the minimum particle diameter required to obtain stable foams being approximately 1.50 μm; stable foams could not be prepared using 1.02 μm PS latex. Wilson’s observations appear to be closely related to the ‘surface coagulation’ phenomenon previously studied by Heller.
and coworkers\textsuperscript{29}, in which colloidal dispersions of low charge density coagulated at an air-water interface after addition of salt. The critical salt concentration required to induce surface coagulation was just less than that required for coagulation in bulk solution\textsuperscript{26}.

Kettlewell \textit{et al.}\textsuperscript{27} have synthesized three types of micrometer-sized PS latexes by the precipitation or dispersion polymerization method using a cationic azo initiator, an anionic persulfate initiator, or the cationic azo initiator in combination with a non-ionic polymeric stabilizer, and the foam stabilization performance of each latex was examined in detail. Below pH 7, two of the three latexes had cationic character: under these conditions, latex concentrations as low as 3.0 wt % were sufficient to generate highly stable foams. The same latexes proved to be ineffective foam stabilizers above their isoelectric points (where they possessed net negative surface charge). In contrast, the permanently anionic PS latex did not produce stable foams under any conditions. Considering that the air-water interface is negatively charged\textsuperscript{28}, it can be considered that the electrostatic attractive force is the driving force for the particle to attach to the air-water interface, and the positively charged particles can be adsorbed to the air-water interface.

Velev and co-workers\textsuperscript{29} described preparation of highly stable foams using polydisperse bisphenol A-based epoxy resin microrods with an average length of 23.5 $\mu$m and an average diameter of 0.6 $\mu$m, in the absence of any surfactant. Due to their rigid, entangled structure and resistance to mechanical perturbation, these microrod-stabilized foams were very stable, even after drying.

### 3.3.2 Sterically-stabilized organic particles

Fujii \textit{et al.}\textsuperscript{30} serendipitously discovered that PS latex particles with diameters ranging from submicron to micrometer, which were synthesized by emulsion and dispersion polymerizations using poly(N-vinylpyrrolidone) (PNVP) as a colloidal stabilizer, can stabilize air bubbles in water by adsorbing to the air-water interface (see Fig. 7a). Such foams can survive for more than two years in a wet state and remain intact even after drying. In contrast, foams stabilized with molecular surfactants such as sodium dodecyl sulphate and PNVP were destroyed after removal of the aqueous phase. Optical microscopy studies revealed hexagonally close-packed arrays of PS particles within the foam (Fig. 7b), which sug-
gests high colloidal stability for the PS particles prior to their adsorption at the air-water interface. This hexagonally close-packed latex arrays in the walls of the dried foam leads to localized moiré patterns (see Fig. 7c) being observed by optical microscopy. Moreover, the dried foams are highly iridescent in bright transmitted light (Fig. 7d), which may offer potential applications in security inks and coatings. Fujii et al. have also reported that poly(methyl methacrylate) particles, poly(4-bromostyrene) particles, and polyacrylonitrile (PAN) particles synthesized by dispersion polymerization using PNVP as the colloidal stabilizer can stabilize foams, but poly(2-hydroxypropyl methacrylate) particles do not stabilize a foam. These results have suggested that the polarity of particles should have an effect on the stabilization of foams.

In order to add smart functions to the foam stabilized with particles, researches have been started on a construction of stimuli-responsive foam system. In order to control the stability of the foam by external stimuli such as pH, temperature, etc. on demand, polymer particles containing stimuli-responsive component were used as the foam stabilizer. In such systems, control of the hydrophilicity and hydrophobicity of the particle surface (control of the wettability relative to the air-liquid interface) by some external stimuli leads to the adsorption of particles to the interface or the desorption from the interface, that is, foam stabilization or defoaming. Binks et al. have constructed a pH-responsive foam system using PS particles coated with poly(acrylic acid) (PAA) as a colloidal stabilizer on the particle surfaces (see Fig. 8). When the pH value of the aqueous media is below pKa of PAA (< pH4.5), PAA colloidal stabilizer on the surface of the particles is protonated and the PS particles have affinity to air: the PS particles can absorb to the air-water interface, hence stable foam was prepared. On the other hand, at pH6 or more, PAA on the PS latex surface is de-protonated and the PS surface has highly anionic character: the PS particles can only disperse in the aqueous media due to the high hydrophilicity and no stable foam was stabilized. In addition, it has been clarified that, by adding alkali to the stable foam that is prepared at low pH, it is possible to destabilize the foam on demand (see Fig. 8). More recently, Dupin et al. have found out that the pH-responsive poly(2-vinylpyridine) (P2VP) microgel particles can work as an effective stimuli-responsive foam stabilizing agent and it is possible to destabilize

![Fig. 7 Optical micrographs of the latex foam prepared using 1.57 μm sterically stabilized polystyrene latex particles. (b) Magnified image that shows hexagonally ordered latex particles at the surface of one of the air bubbles shown in (a). Confocal laser scanning microscopy studies on an individual bubble (see inset shown in Fig. 7a) revealed a red halo, which demonstrates that fluorescently labeled PNVP-stabilized PS particles were adsorbed at the air-water interface, which is a necessary and sufficient condition for stabilization of the air bubbles. (c) Moiré patterns produced by polystyrene latex bilayers as observed by optical microscopy. (d) Digital photographs of polystyrene latex-stabilized foam fragments redispersed in water viewed under transmitted sunlight after annealing at 105 °C for 10 min. Note the iridescence from the fragments. [Quoted from reference 30(a). Copyright, American Chemical Society.]
the foam by the addition of acid.

The particle-stabilized foams have also been exploited as a technology platform for the production of novel porous materials. Fujii et al.31 have succeeded in creating porous carbon materials from the particulate foams. First, PAN latex particles were synthesized by dispersion polymerization as a precursor of carbon materials and prepared the particulate foam using the particles. After drying, the PAN-based particulate foam was heated up to 1000°C in an N₂ atmosphere, which led to porous carbon materials with pore sizes dependent on the original air bubble diameters.

4. Method of Evaluating Foam Stabilized using Particles

4.1 Microscope observation of air bubbles

Optical microscopy is suitable for observation of air bubbles with diameters ranging from micrometer to sub-millimeter in the wet and dry states, and is useful for obtaining the average diameter of the air bubbles. Sample preparation for the optical microscopy study is simple. Confocal laser scanning microscopy (CLSM) is also suitable for observation of air bubbles in the wet and dry states. CLSM studies on air bubbles stabilized with fluorescently labelled particles have revealed halos, which demonstrated that the particles were adsorbed at the air-water interface, which is a necessary and sufficient condition for stabilization of the air bubbles (Fig. 7a inset)30.

4.2 Observation of bubble size and stability of foam

Generally, the foam was observed by the naked eye in order to evaluate the bubble size and their distribution or the stability. Foam columns equipped with glass frits are widely used to generate and characterize foams34. The foam columns were also used in the particulate foam system. Fujii and Armes et al.30 have evaluated particulate foam generation, and stability of the foam against drying, and change in the volume using the foam column. Horozov and Binks35 have developed an automated dispersion stability analyzer (DiStA 24) using a commercially available scanner, and have succeeded in evaluating coalescence and creaming of foams automatically well before it is possible by the naked eye at regular intervals of time.

4.3 Bubble preparation using microchannels

The use of microchannels makes possible not only preparation of bubbles with a uniform size, but also kinetic studies on adsorption of particles at air-water interfaces. Subramaniam et al.36 have used a hydrodynamic focusing device with three channels (one channel for air, and the other two channels for aqueous medium), and have adjusted accurately the size and stability of air bubbles stabilized by particles (see Fig. 9). The air bubbles covered with the particles are formed with good reproducibility only at high flow speeds (10 cm s⁻¹), suggesting that the particles are adsorbed at the interface in a time scale on the order of several tens of microseconds. In addition, by loading particles differentially labelled with rhoda-
mine and fluorescein in the two outer channels of the microfluidic device, it was shown possible to produce hemi-shells, or Janus armour. The ability to assemble two or more types of particles on a single shell is the first step in producing chemically patterned shells that may be useful for targeting or sorting purposes.

5. Water Drops Stabilized by Particles in Air

As already shown in Fig. 1, preparation of water-in-air inverse foam systems has been demonstrated. One example of these systems is liquid marbles. Droplets of polar liquids, such as water, glycerol, ionic liquids, coated by hydrophobic particles show non-sticking behaviour against substrates on which the liquids readily wet without the particle coating.

Aussillous and Quéré reported that liquid marbles could be obtained by making a small amount of liquid (typically between 1 and 10 mm³) roll in a very hydrophobic powder (lycopodium grains of typical size 20 μm covered with fluorinated silanes). The grains spontaneously coat the drop, which can eventually be transferred onto other substrates. Fig. 10a shows a water marble of radius 1 mm, placed on a glass plate (which is wetted by water), where it is observed to adopt a spherical shape. Thanks to the adsorbed grain layers at the liquid-air interface, the wetting between the glass and the water is suppressed. These liquid marbles roll off an inclined plane rather than slide and also can be manipulated by applying external fields such as electric and magnetic fields. Interestingly, these liquid marble can float on a water pool thanks to the hydrophobic particles on the mar-

ble surface (Fig. 10b). Bon and co-workers indicated that a water droplet with a diameter of ca. 5 mm in air could be stabilized with cross-linked poly(divinyl benzene) (PDVB) particles synthesized via precipitation polymerization. The water droplet deviates from a spherical shape and appears oval on the glass plate, as the drop size is greater than the capillary length. Moreover, the evaporation process of the water droplet was investigated and deformation of the colloidal assembly on the air-water interface was observed. The PDVB particles are irreversibly adhered to the air-water interface and the total surface area of the droplet can no longer decrease. The only alternative for the droplet is to change its surface-to-volume ratio, which means it has to deform.

Much smaller water drops (tens to hundreds of micrometer) dispersed in air can be prepared by mixing hydrophobic particles and water at high shear speed by using a food blender or by using a planetary low shear mixer. This water-in-air inverse foam system is termed dry water, as it shows free-flowing powder behaviour as shown in Fig. 1d, reflecting the powdery nature of the particles themselves. The water droplets in the dry water are armoured by the adsorbed hydrophobic particles (DCDMS-modified nano-sized silica particles), which prevent the droplet coalescence (Fig. 10c). Up to 98 wt.% of water can be incorporated into the powder. The dry water would potentially play a carrier of ingredients. By applying shear onto the dry water, for example, rubbing it on skin surfaces, small water drops are forced to coalesce. This leads to appearance of macroscopic

Fig. 9 Production of air bubbles covered with particles by using a three-channel hydrodynamic focusing device. (a) Delivery of 4.9-μm diameter polystyrene particles dyed with rhodamine (yellow) and 4.0 μm particles dyed with fluorescein (green) on an air/water surface. (b) An example of tailored production of an air bubble covered with approximately two hemispheres of different size particles (Janus shell). [Quoted from reference 36. Copyright, Nature Publishing Group.]
water and delivery of ingredients to the skin. In fact, skin whitening products consisting of toner lotion drops stabilized by particles have been already on the market (Benefiance luminizing powder-C essence poudre éclat C whitening, Shiseido). Recently, Cooper et al.\textsuperscript{41} reported that the dry water stabilized with hydrophobic fumed silica nanoparticles is effective in methane storage application. They showed a great increase in the rate of methane uptake in methane gas hydrate by forming the hydrate in preformed dry water powders, comparing with bulk water.

Almost all the liquid marbles described in papers have been composed of either water or glycerol as the liquid and hydrophobized lycopodium, reactive polymer or silica as the stabilizing particles. These particles and liquid are potentially reactive and do not permit the use of organic chemistry; the liquids are volatile. Gao and McCarthy\textsuperscript{42} reported the use of perfluoroalkyl particles (oligomeric and polymeric tetrafluoroethylene, which are unreactive) to stabilize a range of ionic liquid marbles. Ionic liquids are not volatile and have been demonstrated to be versatile solvents for chemical reactions.

6. Conclusion

An overview of foams and liquid marbles (dry liquids) stabilized by the colloidal particles was given. It is considered important to conduct researches on design, preparation, characterization of particulate foams and dry liquid systems using the particles whose surface characteristics are strictly controlled by utilizing particle surface engineering technology. The research for clarifying the correlation between the characteristics of the particles and the characteristics of foams and dry liquids should be also important. Further, it is required to develop foams and liquid marbles systems whose stability can be controlled by physical stimuli (temperature, light, electric fields, magnetic field, etc.), and/or by chemical stimuli (pH, ionic strength, solvent change). In addition, synthesis of functional materials using foams and dry liquids stabilized by particles as templates is also a field of research that will attract a lot of attentions.

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