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Fast Dynamics and Relaxation of Colloidal Drops during the Drying Process Using Multispeckle Diffusing Wave Spectroscopy

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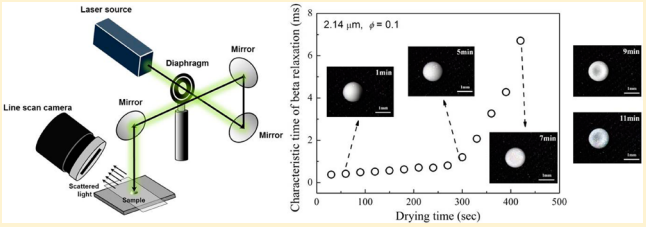
ABSTRACT: The fast dynamics generated by the Brownian motion of particles in colloidal drops, and the related relaxation during drying, which play key roles in suspension systems, were investigated incorporating multispeckle diffusing wave spectroscopy (MSDWS). MSDWS equipment was implemented to analyze the relaxation properties of suspensions under a nonergodic and nonstationary drying process, which cannot be elucidated by conventional light scattering methods, such as dynamic light scattering and diffusing wave spectroscopy. Rapid particle movement can be identified by the characteristic relaxation time, which is closely related to the Brownian motion due to thermal fluctuations of the particles. In the compacting stage of the drying process, the characteristic relaxation time increased gradually with the drying time because the particles in the colloidal drop were constrained by themselves. Moreover, variations of the initial concentration and particle size considerably affected the complete drying time and characteristic relaxation time, producing a shorter relaxation time for a low concentrated suspension with small particles.



I. INTRODUCTION

Suspensions, which are heterogeneous fluids including dispersed solid particles, are ubiquitous in everyday items such as dairy products, cosmetics, cleaning materials, and so on. Understanding their fundamental properties is indispensable for efficient manufacturing and control of related products because suspensions exhibit rather more complicated rheological and dynamic behaviors than simple fluids; these behaviors are attributed to the presence of solid particles. Because of the various industrial applications of suspension systems, numerous theoretical studies have been explored over a long time period[1−5] concerning rheology and transport phenomena, such as paste-like behavior, jamming, or gelation, in suspensions having low to high concentrations.[6−8]

The clarification of the intricate behaviors of solid particles during the drying process has become an issue of interest in academia and in industry.[9−12] A representative example occurring in the drying of a particulate system is the coffee ring effect. Coffee drops on a solid surface leave dense, ring-like deposits of particles along the drop's edge when drying is complete. Deegan et al.[9] eloquently explained the mechanism of this effect, reporting that liquid flows from the center to the edge of a drop, maintaining the drop's shape during drying, because the evaporation flux at the edge is faster than that in the center. As a result, particles in the liquid spontaneously move to the edge by capillary flow, increasing the particle concentration at the edge.

Since then, several methods have been developed to elucidate the properties of colloidal materials during drying.[13−17] Narita et al.[13] reported a variation in α-relaxation, which represents the slow dynamics of particles in a concentrated suspension during drying and wetting using multispeckle diffusing wave spectroscopy (MSDWS). They used a charge-coupled device (CCD) camera to investigate the α-relaxation behavior related to the structural rearrangement of the particles. However, the frame rate of the CCD camera was too slow to detect the fast dynamics of the particles. Xu et al.[15] observed three-dimensional particle movements in a suspension drop during drying using confocal microscopy. Note that the time interval between images captured there was long, so the experiment failed to grasp the fast dynamics, such as Brownian particle motion. In this study, MSDWS is implemented for detecting features due to the rapid motion of particles during drying of a suspension drop.

MSDWS is based on light scattering which has been broadly applied in the field of polymer chemistry to measure the size and molecular weight of polymer chains in dilute polymer solutions.[18−23] In examinations of microstructure, a microscope method is generally involved to visualize the true shapes. However, it is restricted to local observation and cannot provide information regarding an entire sample. By contrast,

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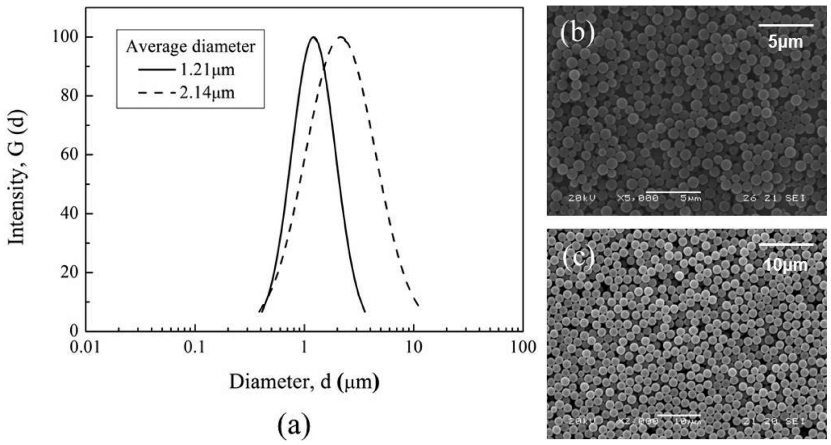

Figure 1. (a) DLS data and SEM images for PS particles with (b) 1.21 μm and (c) 2.14 μm diameters.

scattering methods can reliably scan representative data for an entire sample.

The scattering method called dynamic light scattering (DLS) offers the light intensity autocorrelation function with a lag time, and predicts the degree of Brownian motion of particles in suspension through the concept of diffusivity.[24,25] It is applied only in dilute suspension systems on the basis of single scattering. The hydrodynamic radius of particles can be evaluated with the Stokes−Einstein equation and the diffusivity from the autocorrelation function.

The DWS method, which was pioneered by Pine et al. in 1988 has an experimental methodology similar to that of DLS, but it focuses on more concentrated solutions.[26,27] In other words, DWS is based on multiple scattering. Both DLS and DWS can be applied to an ergodic system because they use a single speckle detector. An ergodic system implies a dynamical one showing the same behavior averaged over time as averaged over space. For analyzing the nonergodic systems, MSDWS incorporating a CCD[19,20] or line scan camera (CMOS) as a multidetector, as described below, is indispensable. Other novel methods have also been suggested, such as the echo speckle imaging (ESI) technique by Zakharov and Scheffold[14] and the two-cell technique.[7]

Most research employing light scattering methods have concentrated on the particle dynamics of suspension systems by α-relaxation. α-Relaxation of particles in a suspension is generally related to the structural rearrangement of particles, whereas β-relaxation is intrigued by thermal fluctuations of particles before their rearrangement. To figure out whole relaxation phenomena of suspension drops, it will be also important to develop scattering technique for β-relaxation behavior related with the fast motion of particles which has not been fully explored.

In this study, we tried to elucidate the dynamics of particles in a nonergodic suspension drop system during a nonstationary drying process using MSDWS. The characteristic time of β-relaxation of particles is regarded as the representative indicator to predict their fast dynamics. As drying proceeds, the relaxation time increases gradually during the compacting stage because particles in a colloidal drop are constrained at the edge of the drop. From the characteristic time for β-relaxation, we could verify the drying state and quantitatively predict the Brownian motion of particles. We further investigated the effects of the initial concentration and size of the particles on the relaxation dynamics of particles in the suspension drop.

II. EXPERIMENTAL DETAILS

A. Preparation of Colloidal Suspensions. To analyze the effects of the particle size and initial concentration of the suspension on the particle dynamics during drying, two types of polystyrene (PS) spherical particles with uniform sizes (average diameters of 1.21 and 2.14 μm) were synthesized by dispersion polymerization method. Styrene monomer was purified by vacuum distillation, and 2,2′-azobisisobutyronitrile (AIBN) was recrystallized from methanol before the use. Polyvinyl pyrrolidone (PVP) with molecular weight of 1 300 000 g/mol was used as polymeric stabilizer. Micron-sized PS particles were prepared in a three-necked double-jacket glass reactor of 500 mL with a slight modification from the previous report.[28] The reactor was equipped with a stirrer, a reflux condenser and a nitrogen inlet. For producing small PS particles, 40 g of styrene, 3.2 g of PVP were taken inside the reactor containing 200 g of ethanol, and 10 g of water. Polymerization was carried out in the presence of 0.4 g of AIBN at 70 °C for 24 h with the agitation speed of 120 rpm. Large PS particles were prepared in the same manner as the procedure for small PS particles except that 200 g of isopropanol instead of ethanol and 1.6 g of PVP were used. The size of PS particles was measured by the SEM (JSM 5200, Jeol, Japan) images and DLS (Brookhaven, USA), confirming homogeneous PS particle size (Figure 1). PS particles were dispersed in water with initial volume fractions (ϕ) of 0.05, 0.1, 0.2, and 0.3. The volume of PS colloidal drop was set to 1 μL so that the incident light covered the entire colloidal drop on a glass plate. The plate offers a proper hydrophobicity making the droplet have a sufficiently large contact angle for the initial semisphere.

B. Multispeckle Diffusing Wave Spectroscopy (MSDWS) Device. MSDWS was originally designed for analyzing the slow dynamics of materials. This technique was revamped here for the fast dynamics of nonergodic materials and the real-time measurement along the drying time. That is, our MSDWS setup was employed to observe the rapid motions of PS particles in a suspension drop during drying, as displayed in Figure 2. Laser light was reflected by several mirrors, and then focused on the entire colloidal drop. The temperature stabilized green laser (Jinsung Laser, DPGL-2200, Korea) used in this experiment is characterized by a 532 nm wavelength, 200 mW output power, 1 mm beam diameter, and beam mode of TEM00. A CMOS line scan camera (Basler Vision Technologies, spL-4096−39km, Germany) with a very high frame rate of 38.5 kHz and 4096 pixels was used as a multiple detector to accurately capture the information of the fast particle movements at the very short lag times in the selected drying steps. The position of the camera (e.g., the distance between the camera and the drop sample, and the backscattering angle) through several tests was optimized in order to maximize the signal-to-noise. Because each pixel of the line scan camera corresponds to a single detector, the camera can be said to represent 4096 detectors. For our experiments, we set the time interval of this camera from 100 to 700 μs. Early in the drying process, a line rate of 100 μs was adopted owing to the rapid

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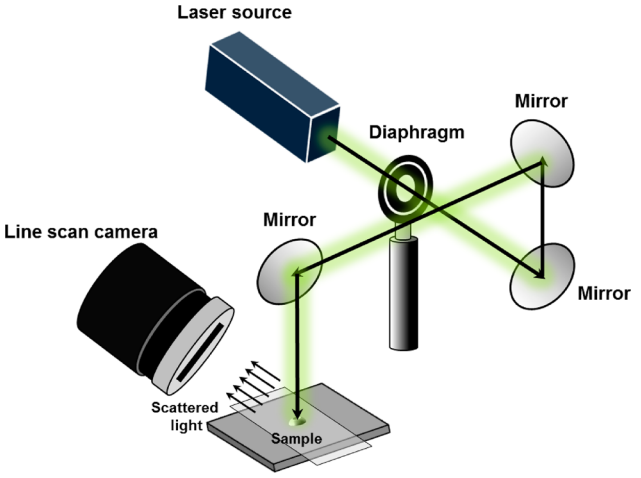

Figure 2. Schematic diagram of MSDWS device.

movements of the particles, and at the last part of drying, a line rate of 700 μs was used to observe particle motions for an extended time.

Although the light scattering technique of MSDWS is similar to that of DLS and DWS, MSDWS differs considerably from them in that it adopts a CCD camera or line scan camera acting as multiple detectors in which each pixel (i.e., detector) of the CCD camera or line scan camera depicts an independent speckle of data. The autocorrelation function, $g_2 - 1$, which indicates the correlation level between the light intensities at two different times, can be obtained by ensemble averaging of N speckles as

$$g_2(\tau_w, \tau) - 1 = \frac{\langle I_n(t_w + \tau) I_n(t_w)\rangle_n - \langle I_n(t_w + \tau)\rangle_n \langle I_n(t_w)\rangle_n}{\langle I_n(t_w + \tau)\rangle_n \langle I_n(t_w)\rangle_n} \quad (1)$$

where I_n is the light intensity at the nth pixel, $\langle \cdots \rangle_n$ denotes the ensemble average over the pixels, and t_w and τ represent the aging time (i.e., drying time) and lag time, respectively. The autocorrelation function measured at each drying time was normalized to make its maximum value 1. Thus, the autocorrelation function for MSDWS can be obtained for a very short time period, indicating the ability to scrutinize particle dynamics in turbid media, i.e., in the nonergodic PS particulate system at aging times t_w during a nonstationary drying process.

C. Experimental Procedures. First, we captured images of the light intensity scattered by particles in a suspension drop using the line scan camera. A typical temporal image is presented in Figure 3a. One pixel in the horizontal direction represents one individual detector, and the vertical direction denotes the passage of time. That is, each pixel in the horizontal direction plays a key role as an independent detector, and each pixel in the vertical direction shows the light intensity at different times. Figure 3b exhibits fluctuations in the light intensity at several pixels with time. The fluctuations result from the particles' Brownian motion. An in-house MATLAB program was implemented to read these fluctuating intensity data and calculate the autocorrelation function; the brightness of the monochrome image was represented by numbers between 0 (perfectly black) and 255 (perfectly white). The averaged intensity of 4096 pixels at a specific time exhibits an almost constant value as illustrated in Figure 3c. Note that the brightness detected by the line scan camera is scattered only by particles, not by other light sources, guaranteeing that the intensity data in our experiments were reliable for analyzing the dynamics of particles in the colloidal drop. Ten-fold experiments were repeatedly conducted under given conditions (particle size and concentration), and the scattering images for 1 s lag time were captured every 30 s until the drying was completed. The ambient temperature and humidity near a droplet should be carefully controlled to 26 ± 0.5 °C and 50 ± 3%, respectively.

III. RESULTS AND DISCUSSION

The effects of the initial volume fraction and particle size of PS in a colloidal drop, on the particle dynamics during drying, were examined. Figure 4 shows the autocorrelation function (g_2−1) data of suspensions with PS particles (1.21 μm in size) at different initial volume fractions [(a) ϕ = 0.05, (b) 0.1, (c) 0.2, (d) 0.3] and at different drying times. The autocorrelation function decreased with the lag time and increased with the aging time and initial volume fraction. Its increase with the aging time implies that the movements of particles were highly

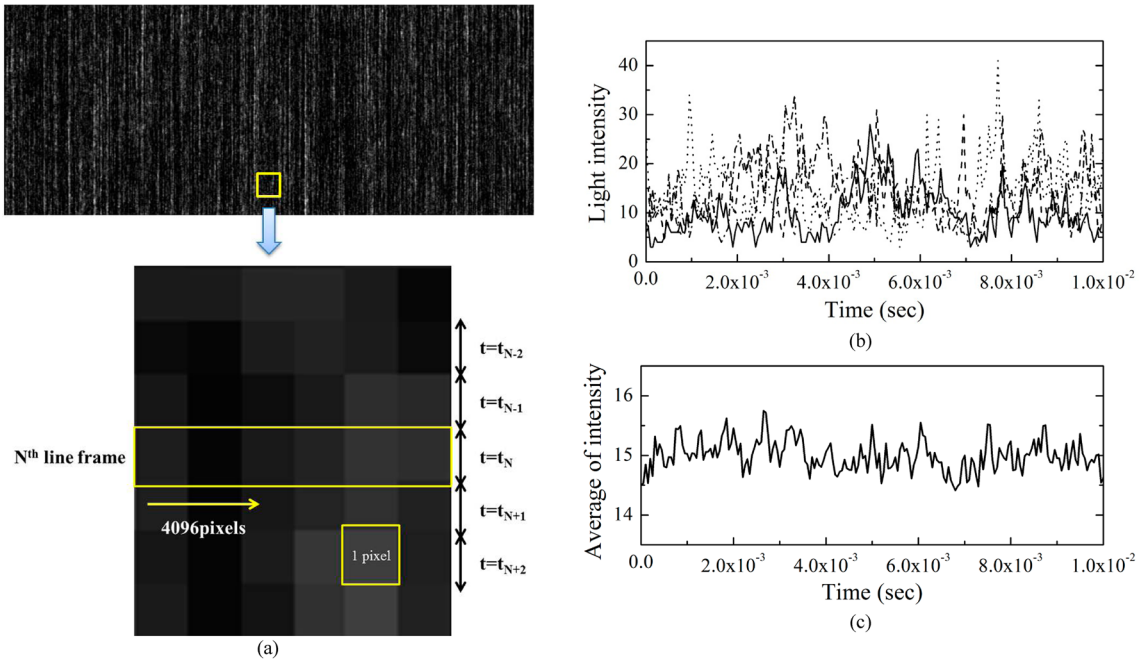

Figure 3. (a) Typical temporal speckle image obtained by line scan camera, (b) light intensity data at several pixels with time, and (c) ensemble average of light intensity with time.

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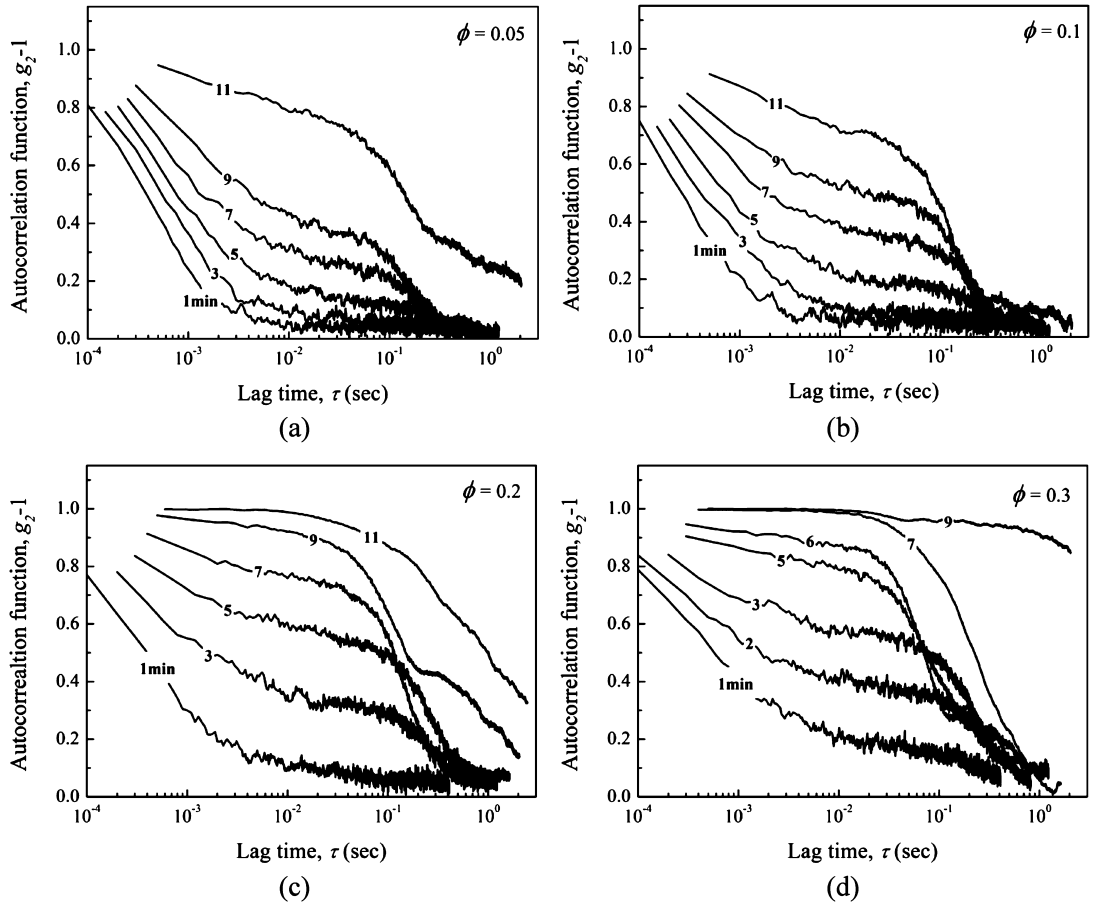

Figure 4. Autocorrelation function under particle diameter of 1.21 μm and several initial volume fractions: (a) 0.05, (b) 0.1, (c) 0.2, and (d) 0.3.

correlated, in contrast to the case at a low aging time. As the dispersive media evaporated, the particles became compact, and their motions were constrained after the appropriate amount of aging time. Similarly, a high volume fraction of PS particles yields a high degree of correlation among the particles.

To quantify the fast motion of particles with respect to the drying time, the concept of the characteristic time of β-relaxation was adopted.[13,19,29] Colloidal suspensions exhibit two distinctive particle relaxation mechanisms: a fast one called β-relaxation and a slow one called α-relaxation. β-Relaxation is closely related to Brownian motion resulting from thermal fluctuations of particles, whereas α-relaxation corresponds to the collective rearrangement of particles above the critical concentration. In this system, the characteristic time of β-relaxation, τ_β, is arbitrarily defined as the time at which the value of the autocorrelation function becomes 0.6, as in the cases of Narita et al.,[13] Viasnoff et al.,[19] and Viasnoff and Lequeux.[29] A line scan camera with a fast line rate is a good tool for detecting β-like relaxation.

As depicted in Figure 4, intricate patterns of autocorrelation function data are generally divided into two regions along the time scale. In a short lag time region ($\tau < 10^{-3}$ s), the autocorrelation function is dominantly influenced by the fast particle motions related to the Brownian motion. In a rather long lag time region (0.1 s < τ < 1 s), it is connected with the slow α-relaxation of particles. Considering the evolution of autocorrelation functions along the drying time, β-relaxation of particles will be dominant in the early drying stage. Like the coffee ring effects, particles move toward the edge of drop during drying (Figure 5). In the middle stage of drying, both β- and α-relaxations will be influential together. In other words, particles are migrated toward drop edge by capillary flow and compacting motion as well as Brownian motion in a suspension drop. In the last stage of drying, particle dynamics will mainly follow α-relaxation because the suspension drop will become highly concentrated beyond the critical concentration. Locally packed particles are slowly moved by the structural rearrangement. Here, the fast dynamic features by the β-relaxation are only emphasized.

Figure 6 shows the characteristic times of β-relaxation, τ_β, during drying for particles of 1.21 and 2.14 μm in a colloidal drop under several initial concentration conditions of ϕ = 0.05, 0.1, 0.2, and 0.3. As explained above, τ_β was determined within the short lag time regime where the Brownian motion of particles is dominant. It is worth mentioning that there will be little crystal-like phase within a colloidal drop in Figure 6 because the characteristic times defined here, as an indicator of β-like relaxation, were determined from the autocorrelation function curves decayed to almost zero value, judging from the results by Pusey and van Megen.[30]

The variations of τ_β during drying directly indicate the effects of drying on the fast motion of particles. τ_β rises with the drying time, reflecting the increase in the autocorrelation function. During the drying process, the volume fraction of a colloidal drop increases steadily. Thus, particles' fast movement becomes restricted, and τ_β increases constantly in the compacting stage.

Effects of initial concentration and particle size on the characteristic relaxation time of particles can be interpreted as

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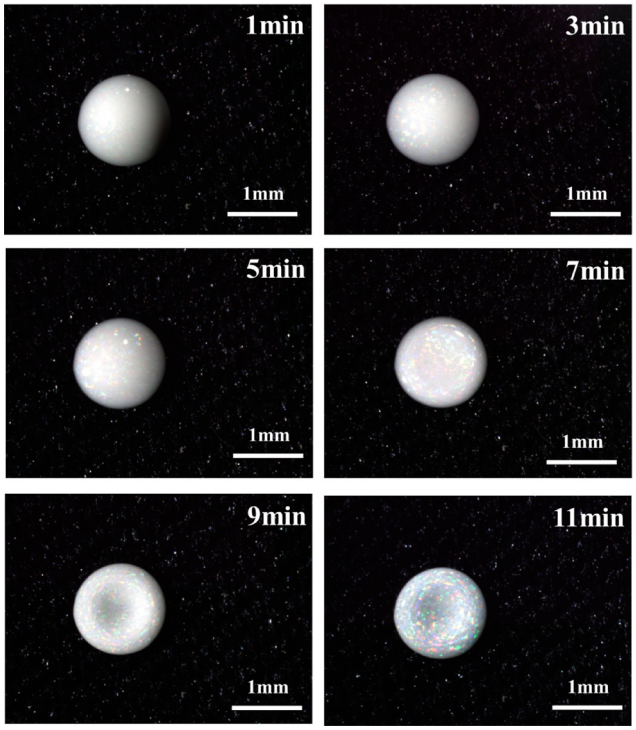

Figure 5. Drying pattern of a suspension drop (2.14 μm, ϕ = 0.1).

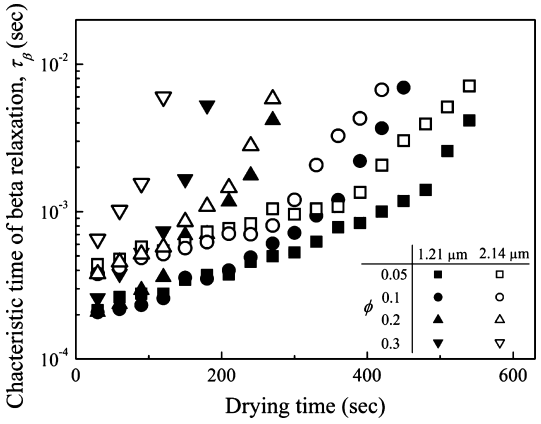

Figure 6. Characteristic time of β-relaxation under particle diameters of 1.21 μm (closed symbols) and 2.14 μm (open symbols) and several initial volume fractions.

follows: First, evolutions of τ_β with the drying time under several initial concentrations are compared. The relaxation time of particles increased gradually in the incipient drying and then grew greatly in the middle stage of drying owing to the dense packing and thus restricted movement of particles. Also, a higher initial concentration yielded a higher τ_β in the initial drying stage, resulting from the slow Brownian motion of particles in more limited free volume. Second, the effect of particle size (1.21 and 2.14 μm) at a constant initial volume fraction is taken into account. The τ_β value for small particles is generally lower than that for large particles until the middle of drying time since the small particles demonstrate the rapid Brownian motion. Note that Brownian motion is closely related to the diffusion coefficient of particles (in inverse proportion to particle size), which can be determined using the Stokes–Einstein relation. That is, a large particle size reduces the diffusivity, making τ_β increase.

To further shed light on the relaxation dynamics of particles from autocorrelation function data, their values at the fixed short lag times (1 ms and 5 ms) have been compared in Figure 7. A high concentrated colloidal drop has large value of

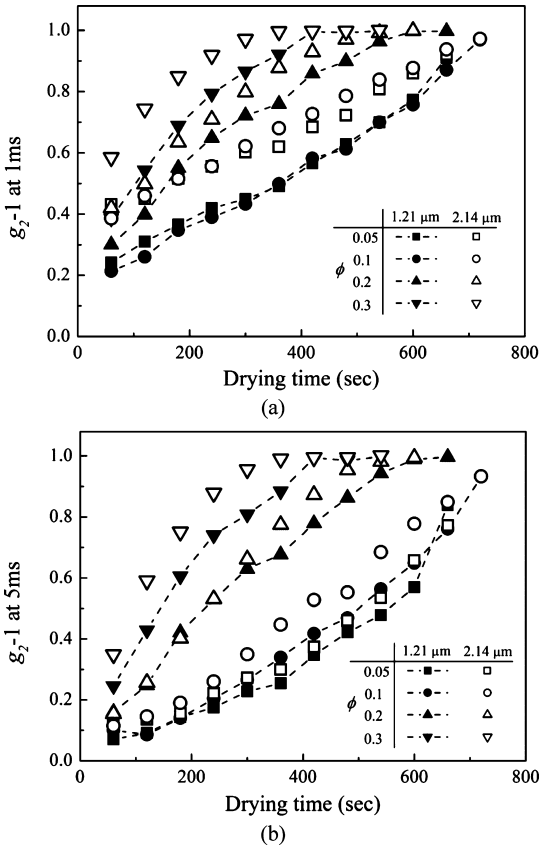

Figure 7. Comparison of the autocorrelation function data at the fixed short lag times ((a) 1 ms and (b) 5 ms).

autocorrelation function, representing that particles are considerably correlated due to their slow fluctuation. As the particle size and initial condition increase, the drying time for approaching the highly correlated state at short lag times became shorter. It is also found that autocorrelation function data at low concentrations under the fixed particle size condition were relatively similar from the fact that the particle cluster surrounding other particles does not severely disturb the spontaneous motion of each particle.

IV. CONCLUSIONS

The fast dynamics of particles in a PS suspension drop during drying was investigated using MSDWS, which is one of the most useful methods for analyzing nonergodic and nonstationary systems. By adopting the high frame rate of line scan camera and using the data on the intensity of light scattered by particles within a colloidal drop, the autocorrelation function, $g_2 - 1$, and characteristic time of β-relaxation, τ_β, were evaluated during drying. Relaxation patterns caused by Brownian motion of particles in a colloidal drop were compared for different initial concentrations and particle sizes. The τ_β value was lower for particles with a lower initial concentration because particles under a high initial concentration could be more restricted. In contrast to the case of large particles in a colloidal drop, small particles result in a low τ_β owing to their fast Brownian motion

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in the early drying stage. The characteristic time obtained from the autocorrelation function is found to be a useful indicator for discerning fast particle dynamics in a colloidal drop exhibiting distinctive drying stages.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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