

Dynamics of intermediate to late stage concentration fluctuations during free diffusion experiments

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ABSTRACT

Two experiments were performed using shadowgraph visualization technique in order to study the dynamics of concentration fluctuations. Our experimental setup includes an objective attached to the CCD camera to increase the field of view. Using two colloidal suspensions, one with gold and the other with silica colloid, we extracted both the structure factors and the correlation time during the intermediate to late stages of concentration fluctuations during a free diffusion experiment. The temporal evolution of fluctuations is qualitatively investigated using recursive plots and spatial-temporal sections of fluctuating images. Our experiment reveals significant differences between concentration fluctuations induced in silica and gold colloids. The difference is explained not only in terms of the particle size but due to the possible plasmonic interaction between gold nanoparticle and the incident light.

Keywords: concentration fluctuations, nanocolloids, free diffusion

1 INTRODUCTION

Equilibrium fluctuations in fluids, and binary mixture were investigated in the past both on Earth and under microgravity conditions using different light scattering techniques [1, 2, 3, 4]. Recent experiments have shown that non-equilibrium fluctuations exists during a free diffusion process in liquid mixture and are caused by a coupling between velocity fluctuations and the macroscopic concentration gradient established between two liquids [5, 6]. It has been shown that gravity suppressed the long wavelength fluctuation below a certain cutoff value. As a result, some experiments were carried out in microgravity to investigate the interplay between the gravity and diffusion in fluctuating interface of miscible fluids.

In this paper, we present experimental results regarding the intermediate to late stage of free-diffusion in silica and gold nanocolloids. We were interested in establishing a time frame for the concentration fluctuations. We definitely know that large scale giant fluctuations are present in recordings done during the late stages at 50000 s or 100000 s [6, 7], but when do they actually develop? Our experimental setup include an objective focused on the free diffusion layer that in order to observe and analyze the evolution of fluctuations. Our image processing technique used sets of 1000 images [8]. However, we repeated our analyses for sets that were 250 s apart to capture any possible change in the structure factor and investigated the evolution of fluctuations.

2 EXPERIMENTAL SET-UP

We studied the evolution of the wavelength fluctuations in silica and gold colloids. Our optical setup of a free-diffusion experiment is schematically represented in Fig. 1. A water-soluble colloid was confined in a Hellma 120-OS-20 cylindrical glass cell, 2.0 cm diameter and 2.0 cm height with plane-parallel optical glass windows [7, 8]. The interface between the two fluids was perpendicular to the gravitational field. A denser colloid (silica or gold) was slowly injected using a bent needle at the bottom of the cell completely filled with degassed water. The two fluids are initially separated by a sharp horizontal interface localized almost in the middle of the diffusion cell. A parallel beam of light from a 10 mW He-Ne laser, with a wavelength of 635.5 nm, was collimated and passed vertically upward through the diffusion cell. A progressive scan SONY CCD camera, with sensor area of 5.8 mm x 4.92 mm and a pixel resolution of 4.65 μm , and a Video Lens-10X objective were used for image recording.

We used two different liquids mixture: 1) silica colloids with the average diameter of particles of 200 nm, and 2) gold nano colloids with the average nano-particle of 20 nm. Our results showed that the density concentration fluctuations causing local perturbation in the intensity of transmitted and scattered light cover both gravitational and diffusion effects. Using our experimental data, we were able to analyze the structure factor and their corresponding power spectra for different wave vectors and the correlation time from intermediate to late stage.

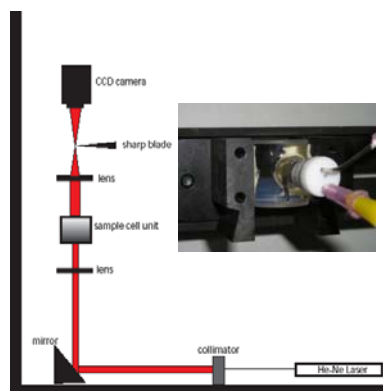


Figure 1. Schematic representation of the experimental setup (left) and a picture of the sample cell unit (right) used to study the giant fluctuations determined by diffusion in a mixture of silica (bottom) and water

3 METHOD

We applied a dynamic light scattering algorithm to study intermediate to late stage concentration fluctuations in a free diffusion experiment in silica and gold colloids. The

full description of the experimental set-up is described elsewhere [8]. The first step in applying the dynamic algorithm was to normalize each image by dividing each image to its spatial average (noted $\langle \rangle$), in order to reduce the effect of variable light intensity [7, 8]:

$$i(\mathbf{x}, t) = I(\mathbf{x}, t) / \langle I(\mathbf{x}, t) \rangle, \quad (1)$$

where $I(\mathbf{x}, t)$ is the two-dimensional image intensity cropped from a snapshot of the sample cell unit, and $\langle I(\mathbf{x}, t) \rangle$ is the spatial average over all pixel positions in the image $I(\mathbf{x}, t)$. The second step is to find the fluctuation image, which is defined as the difference between two normalized images separated by a delay time Δt :

$$\delta i(\mathbf{x}, t, \Delta t) = i(\mathbf{x}, t + \Delta t) - i(\mathbf{x}, t). \quad (2)$$

The third step is to calculate the spatial two-dimensional Fast Fourier Transform (FFT2) for each fluctuation image in order to find the power spectrum of each fluctuating image:

$$\delta i(\mathbf{q}, t, \Delta t) = \text{FFT2}(\delta i(\mathbf{x}, t, \Delta t)). \quad (3)$$

The fourth step consists in computing the time-dependent structure function $c_m(\mathbf{q}, t, \Delta t)$, which is the temporal average of all power spectra in a set of images with a fix delay time Δt :

$$c_m(\mathbf{q}, t, \Delta t) = \overline{|\delta i(\mathbf{q}, t, \Delta t)|^2}_t. \quad (4)$$

One of the characteristics of the power spectra is the azimuthally symmetry and using this property we computed the radial average of structure function $C_m(q, t, \Delta t)$.

$$C_m(q, t, \Delta t) = \overline{c_m(\mathbf{q}, t, \Delta t)}_{|q|.} \quad (5)$$

The structure function $C_m(q, t, \Delta t)$ is related to the sample structure factor $S(q, t)$, the temporal autocorrelation function $G(q, t, \Delta t)$, and the background noise $B(q, t)$ as follows [24]:

$$C_m(q, t, \Delta t) = 2\{[S(q, t)T(q)] \cdot [1 - G(q, t, \Delta t)] + B(q, t)\}, \quad (6)$$

where the shadowgraph transfer function is $T(q) = 4\sin^2(q^2 z / 2k)$, with z the distance from the sample to the CCD, q the wave vector and k the vacuum wave vector of the incident light. The correlation function specific for thermal fluctuations is given by [9]:

$$G(q, t, \Delta t) = \exp(-\Delta t / \tau(q, t)), \quad (7)$$

where $\tau(q, t)$ is the correlation time of thermal fluctuations. By fitting the radial average of the time-dependent structure function $C_m(q, t, \Delta t)$ with the equations (6) and (7), we determined $S(q, t)T(q)$, $\tau(q, t)$ and $B(q, t)$. The two signals, $S(q, t)$ and $T(q)$, obtained with this method cannot be separated using image processing techniques and we will refer to $S(q, t)T(q)$ as the structure factor.

The correlation time is defined as the lifetime of the thermal fluctuations. The correlation time of non-equilibrium fluctuations is given by: [8, 10]

$$\tau_c(q, t) = \frac{q^2}{D(q^4 + q_c^4)}. \quad (8)$$

4 RESULTS

4.1. Silica nanocolloids

We expect a very slow relaxation of nonequilibrium fluctuations for silica due to large nanoparticle sizes. The structure factor versus wave vector (Fig. 2) shows power law dependence for large (170 a.u. $< q < 230$ a.u.) wave vectors. The exponent of the power law decreases from -4.1, which indicated giant concentration fluctuations at the beginning of the relaxation process, down to -2.5 after 100 hours (Fig. 2).

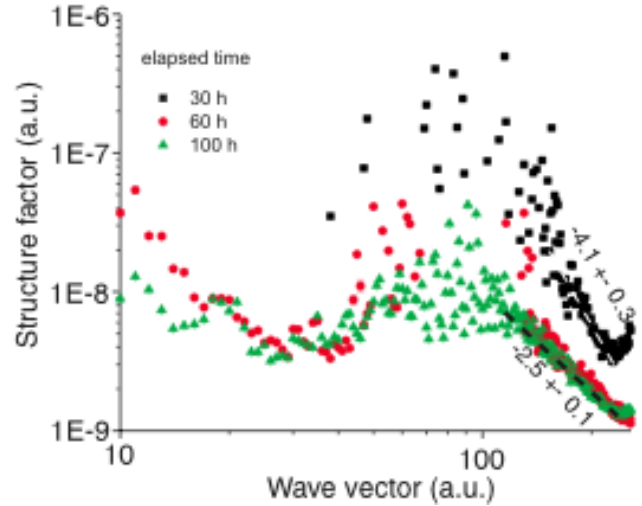


Figure 2. Structure factor for silica at 100 hours elapsed time has a power law exponent of -2.5 ± 0.1 and $\chi^2/\text{DoF} = 1.1549\text{E-}18$, and a coefficient of confidence $R^2 = 0.85$. After 60 h, the exponent is -2.6 ± 0.1 , $\chi^2/\text{DoF} = 1.7086\text{E-}19$, $R^2 = 0.88$. At 30 h, the exponent of the power law is -4.1 ± 0.3 , $\chi^2/\text{DoF} = 2.2357\text{E-}18$, $R^2 = 0.73$.

The correlation (delay) time has the characteristic shape described by Eq. (8). For large wave numbers ($q > 100$ a.u.), the exponent of the power law is around -2.0 with small variations. This is a characteristic signature of concentration fluctuations under gravitational relaxation regime.

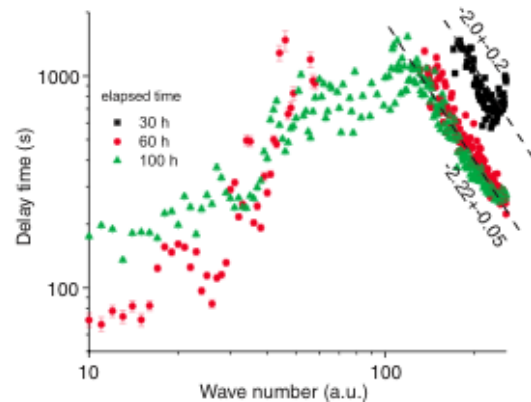


Figure 3. After 100 hours, the diffusion coefficient is $D = 5.4952\text{E-}8 \pm 1.3825\text{E-}9 \text{ cm}^2/\text{s}$, $q_c = 93 \pm 1$ a.u. with $R^2 = 0.78$. Power law exponent of delay time for large q is -2.22 ± 0.05 , with $R^2 = 0.93$. After 60 h, the diffusion coefficient is $D = 4.984\text{E-}8 \pm 1.1814\text{E-}9 \text{ cm}^2/\text{s}$, $q_c = 87 \pm 1$ a.u., $R^2 = 0.8$. For 30 h $D = 2.4601\text{E-}8 \pm 4.6227\text{E-}10$

cm^2/s , $q_c = 13.24249 \pm 0.37315$, $R^2 = 0.64$. After 30h, the power law exponent for large q is -2.0 ± 0.2 .

4.2. Gold nanocolloids

Gold particles used in this experiment were one order of magnitude smaller than silica. As a result, the expected relaxation time is much shorter for this nanocolloid. The structure factor (Fig. 4) has the same shape as for silica (Fig. 2). The exponent of the power law decreases from -3.6 at the beginning of the experiment to almost -2 after 40 hours or recording. Large power law exponents are signatures of giant concentration fluctuations and a -2 exponent is a signature of Brownian fluctuations.

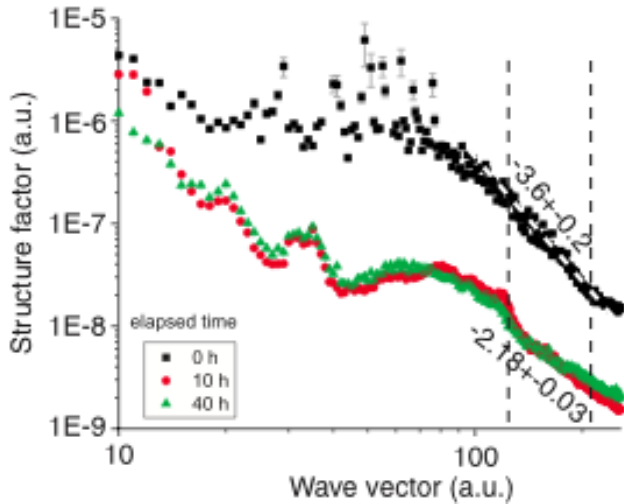


Figure 4. After 40 h, the slope is -2.18 ± 0.03 with $R^2 = 0.98$. After 10 h, the exponent of power law is -2.73 ± 0.04 , $R = 0.98$. Initially the exponent of power law was -3.6 ± 0.2 , $R = 0.87$.

The correlation time follows expected concentration fluctuation Eq. (8). The power law exponent for large wave vectors is -1.54 . However, as diffusion progresses, the correlation time becomes almost independent of the wave vector.

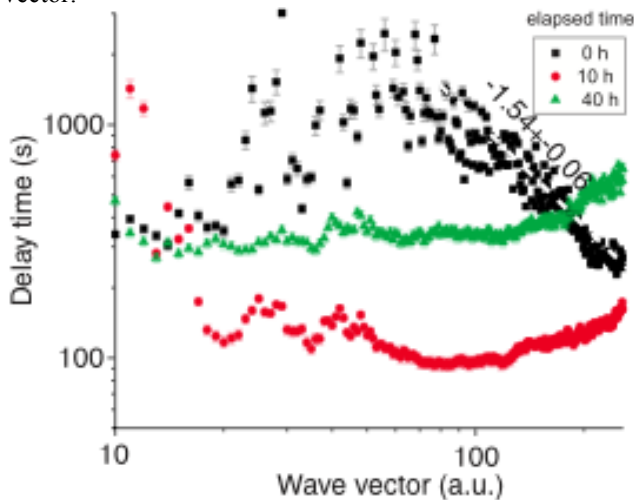


Figure 5. The correlation (delay) time for gold nanocolloids. Initially, the power law exponent for large wave numbers is -1.54 ± 0.06 with $R^2 = 0.85$. The coefficient of diffusion was measured as $9.4139\text{E-}8 \pm 3.6048\text{E-}9 \text{ cm}^2/\text{s}$, the critical wave number was $58 \pm 1 \text{ a.u.}$ with $R^2 = 0.60$.

5 CONCLUSIONS

It has been shown that the structure factor $S(q)$ is the ideal tool in describing fluctuations in a fluid stressed by temperature or concentration gradient. $S(q)$ measurements suggested that giant fluctuations are long-range correlated [1, 3, 7, 8] and they are proportional to the gradient that generated them [5].

We performed free diffusion experiments using 200 nm silica colloids and 20 nm gold colloids to investigate the contribution of different processes (viscosity, gravitational field, and concentration gradients) on the fluctuations of light intensity (Fig. 1).

Our results showed that the power spectra have characteristic rings determined by the shadowgraph transfer function $T(q) = 4 \sin^2(q^2 z / 2k)$, where k is the vacuum wave number for incident light, z is the distance between the CCD camera, the fluctuating interface, $q = 2nk \sin(\theta/2)$, is the scattering wave vector, and θ is the scattering angle. We used a FFT algorithm to compute the power spectra with 512 discrete values for wave numbers in arbitrary units (a.u.). Since the power spectra present azimuthal symmetry, averages over constant wave number values were computed in order to extract the scalar azimuthal structure function $C_m(q, t, dt)$, which is the power spectrum when plotted versus wave vector for fixed delay time dt . The power spectrum measures the intensity of fluctuations in the wave vector domain for a fixed value of delay time dt . The same information is conveyed by the scalar structure function $C_m(q, t, dt)$ in the temporal domain of delay times dt for fixed values of the wave vector q . The advantages of using the scalar structure function $C_m(q, t, dt)$ over the more traditional correlation function allowed us to a) obtain both the structure factors and the correlation time with only one sweep of the data, and b) eliminated any slow drifts in the recorded signal [8, 9]. We used a dynamic method to extract the structure factor $S(q)T(q)$, the correlation time $\tau(q)$, and the background noise $B(q)$ from fluctuation images.

Based on a detailed analysis of the slopes of the structure factor $S(q)T(q)$, we were able to observe giant concentration-induced fluctuations signaled by a slope of about -4 for during the early stages of the relation process (Figs. 2 and 4). During the early stages of the experiment, both for silica (Fig. 3) and gold (Fig. 5), the correlation time has a convex shape well approximated by classical theory encapsulated in Eq. (8). By fitting the correlation time with Eq. (8) we estimated the diffusion coefficient D for both nanocolloids and the corresponding critical wave vector at which the fluctuation due to viscosity (small wave vectors)

is replaced by large gravitation-driven fluctuations. We identified at least two possible causes for the large variability of the exponent of the power law for correlation time: 1) at low wave vectors, the azimuthal average is performed over a very small number of configurations leading to large errors and 2) the maximum point of the correlation time plot, which determines the critical wave vector, shifted over time towards smaller values according to the power law $q_c \propto t^{1/8}$ derived from (3). Our results are in good agreement both with theoretical predictions [7] and with other experiments [10]. For silica, giant concentration fluctuations are still observed even after 30 hours as indicated by the large value of the power law exponent in the structure factor (Fig. 2). However, for gold nanocolloids, even after 1 hour the power law exponent is down to -3.6 and converges very fast to -2, which indicates Brownian motion. At the same time, the correlation time of concentration fluctuations is almost independent of the wave vector (Fig. 5).

ACKNOWLEDGMENTS

This research was supported by a R&D grant from the College of Charleston to A. Oprisan and S. A. Oprisan. We are grateful to Dr. Fabrizio Croccolo for fruitful discussions both on experimental details of shadowgraph setup and the numerical implementation of the dynamic method.

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