Time-scale dependent Brownian motion of nanoparticles in clusters at a solid-liquid interface by laser trapping

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Abstract. Nanoparticles in a cluster trapped by laser-induced force field show Brownian motion at solid-liquid interfaces. The cluster formation means that the particles are highly concentrated. In general, the diffusion coefficients of particles in fluids decrease with substantially high concentration and also in the vicinity of solid walls due to the hydrodynamic effect. The particle trajectory data obtained from the experimental measurements show that the longer time span of observation leads to smaller diffusion coefficient due to the confinement effect. However, they also exhibit higher diffusion coefficient compared to the the bulk condition when evaluated at a sufficiently short time span of the frame interval under the condition of sufficiently high laser powers.

1. Introduction

Laser-induced force field causes colloidal particles in liquid in the vicinity of a solid wall to form clusters. The constituent particles do not necessarily form rigid crystal structures but retains Brownian motion. On the one hand, the position of nanoparticles in the clusters changes from arbitrarily defined initial position in a steady state. On the other hand, these particles are trapped in the laser-induced force field, which means that the particles are confined in a finite domain. When the trapping energy is sufficiently large, diffusion coefficient will vanish in the evaluation with the infinite time span. However, as far as the relative positions of particles in clusters changes in time, a kind of diffusion coefficient can be discussed, paying attention to the time scale of the observation. The combination of Brownian motion and optical force field can give rise to diverse dynamical phenomena. As the thermal fluctuation is the essential characteristics of the system, it has also been proposed to combine with light-induced force to transport nanoparticles [1]. The fluorescence correlation spectroscopy (FCS) [2] and related fluorescence detection approach [3] have been employed to measure the trapping dynamics, sometimes being combined with the independent numerical analysis to compare with and understand the measurement data. A confined motion by optical tweezer has been attempted to be evaluated using a numerical analysis [4]. In this article, we discuss the generalized diffusion
characteristics [5] of particles in clusters at a solid-liquid interface by laser trapping. Although
the system of interest is rather one of the typical setups in the laser trapping studies, there are
complexities with respect to the Brownian motion. The particles are highly crowded because
of the trapping, and the particles are in the vicinity of a solid wall, which can slow down the
Brownian motion by the hydrodynamic effect [6, 7]. We try to evaluate the dynamics purely
from the measurement data without introducing too much assumption, which is realized by the
particle tracking analysis from the microscopy movie data [5, 8, 9]. Consequently, we reveal
the emergence of enhanced stochastic motion in the cluster of nanoparticles for sufficiently high
laser powers. A simple protocol for the detection of multiple modes of stochastic motion plays
an important role in this finding [8, 9].

2. Methodological details

2.1. Experimental setup for observation
A 1064-nm near-infrared laser beam from a continuous wave Nd:YVO₄ laser was used for
optical trapping. These lasers were introduced to an inverted microscope and focused on the
surface of the cover slip that constitutes an 86-μm thick container of nanoparticle suspensions.
The objective lens was ×60 magnification, and the images were captured by an EMCCCD
camera. The exposure time and frame rate were 25 ms and 38.1 frame/s, respectively. All
laser experiments were performed at room temperature around 19-22°C. Fluorescent dye-doped
polystyrene nanoparticles with a diameter of 500 nm (F8812, Thermo Fisher Scientific) were
diluted in distilled water to 3 × 10⁹ particles/mL.

2.2. Analysis of the movie data
The irradiated lasers attract the nanoparticles at around the focal point and form nanoparticle
clusters. We extracted the particle trajectories data from the obtained microscopy movie using
the algorithm of Ref. [10]. Then, we analyzed the set of trajectory data based on the framework
of the generalized diffusion coefficient as follows:

\[ \langle |\Delta r(t)|^2 \rangle = 2n_{\text{dim}} \alpha t^\beta, \]

where \( \langle |\Delta r(t)|^2 \rangle \) is the mean squared displacement, \( \alpha \) and \( \beta \) are the coefficient and exponent of
the generalized diffusion, and \( n_{\text{dim}} \) is the dimensionality (i.e., \( n_{\text{dim}} = 2 \) in this article discussing
two dimensional data of \( \Delta r(t) \)). Note that we used the data in the steady state after the
transient period of cluster formation. In the case of normal diffusion with diffusion coefficient
\( D \), the exponent is \( \beta = 1 \), i.e., the MSD evolves linearly as a function of time. Then, \( \alpha = D \)
and hence

\[ D = \frac{1}{2n_{\text{dim}} t} \langle |\Delta r(t)|^2 \rangle . \]

3. Results and discussion
Fig. 1(a) shows the mean squared displacements (MSDs) of nanoparticles in clusters as a function
of time for different laser power conditions. The MSDs increase for a time scale of a second,
and the scaling behavior appears to be the same for different conditions of the laser power.
Nevertheless, there is a dependence of MSD on the laser power in that the higher power causes
larger MSD. Because the higher power for the trapping is likely to cause more tight trapping
that can cause the slower diffusion, there must be the driving effect of the laser on the particles.
For example, the radiation pressure of the laser is attributed to be part of the mechanism of the
enhanced Brownian motion under the concentrated condition.

The MSDs as a function of time can be understood from the framework of the generalized
diffusion coefficient represented by Eq. 1. Defining the initial values of fitting parameters
\( \alpha = \langle |\Delta r(t)|^2 \rangle/(4t) \) and \( \beta = 1 \) respectively, the nonlinear fitting (based on gnuplot ver.4.6)
Figure 1. Time evolution of the particle dynamics obtained from the set of trajectory data: (a) mean squared displacements of nanoparticles in clusters as a function of time for different laser power conditions, and (b) diffusion coefficient as a function of time span to observe the Brownian motion. The particles within 2 \( \mu m \) distance from the laser focal point is defined as those that belong to the cluster. The legends show the laser power to trap the nanoparticles.

yields \( \beta = 1 \) for all cases within the time span of a few seconds. Thus, we use Eq. 2 hereafter. Fig. 1(b) shows the diffusion coefficient as a function of time. There is a common feature that the diffusion coefficients decrease as a function of the time span of observation. This is mainly attributed to the confinement caused by the trapping force fields. On the other hand, the diffusion coefficients depend on the laser power at a fixed time span of observation. The normal diffusion coefficient of 500-nm spherical particles dilutely dispersed in water in bulk can be predicted as \( 8.5 \times 10^{-13} \) m\(^2\)/s based on the Stokes-Einstein relation. At the smallest time scale available in the experiment, which is more free from the confinement effect, the conditions of laser power less than 10 mW correspond to this value. The higher laser power results in the higher diffusion coefficient. In other words, the sufficiently high laser power enhances the diffusion. This is counterintuitive considering only the conservative force field.

However, the optical force does not really consists of the conservative force field alone. The non-conservative component of the optical force can trigger the enhanced Brownian motion. Fig. 2 shows the distribution of displacements in a unit of diffusion coefficient \( D \) at the time span of frame interval \( \Delta t = 0.026 \) s, displayed by the logarithmic scale. This logarithmic representation reveals the possible multiple modes of Brownian motion [8]. In general, the apparent multiple modes can also originate from the error in the tracking analysis [9]. However, Fig. 2 shows the clear dependence of characteristics on the laser power. The results indicate that the enhanced Brownian motion is triggered by the sufficiently high laser power. Although our set of experimental conditions is not likely to induce thermal convection, the non-conservative force, typically the scattering force, incessantly drives the nanoparticles in the direction that approaches the solid wall. The driven nanoparticles repeatedly collide with the solid wall and adjacent particles. This triggering combined with the stochasticity can induce the enhanced stochastic motion. Substantially higher diffusion coefficients in the systems coexisting with convection compared with those without convection have been reported independently from the context of optical force [11, 12], which is of more relevance in the vicinity of a solid wall [13].
Figure 2. Distribution of displacements in a unit of diffusion coefficient $D$ based on an assumption of normal diffusion at the time span of frame interval $\Delta t = 0.026$ s, displayed by the logarithmic scale. This logarithmic representation reveals the possible multiple modes of Brownian motion [8, 9]. The normal diffusion coefficient of 500 nm spherical particles dilutely dispersed in water in bulk can be predicted as $8.5 \times 10^{-13}$ m$^2$/s based on the Stokes-Einstein relation. The legends show the laser power to trap the nanoparticles.

4. Concluding remarks
Nanoparticles in laser-induced clusters at a solid-liquid interface show Brownian motion that is markedly different from the bulk free condition. On the one hand, the confinement effects cause the diffusion coefficients decreasing with the increase of the time scale of observation. On the other hand, in spite of this confinement effect and the location in the vicinity of the solid wall, the Brownian motion is enhanced by the laser. The higher laser power causes the higher diffusion coefficient compared to the bulk free condition at sufficiently short time scale.

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