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Short communication

Simultaneous measurement of size and density of spherical particles using two-dimensional particle tracking analysis method

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ABSTRACT

The motion of spherical particles in liquid phases was investigated using a two-dimensional particle tracking analysis (2D-PTA) method. The analysis of four different materials with this method revealed two different types of particle movements occurring simultaneously: Brownian diffusion and sedimentation. When these two different displacements occurred simultaneously, in the case of particles with a larger size or higher density, the sedimentation displacements were significantly faster than those associated with Brownian diffusion. The occurrence of a faster sedimentation compared to the Brownian diffusion severely affects the accuracy of size determination using PTA methods, as these approaches are based on the Stokes-Einstein relationship, in which the size of a particle is inversely proportional to its Brownian diffusion coefficient. In addition, we successfully demonstrated, for the first time, the potential of the novel PTA method for simultaneously determining the particle size and identifying the constituent material of a limited range of silica and gold particle sizes. The present method may play an important role in the development of new industrial and biological applications of materials.

1. Introduction

The physicochemical and functional characteristics of materials are usually dependent on their size; therefore, the control of the size of a material is a crucial aspect for its industrial and biotechnological applications [1–7]. For example, the catalyst particles used in photocatalysis applications must possess a large surface area, which is crucial for the adsorption and decomposition of organic pollutants by the photocatalyst, and thus for its reactivity. In addition, in the context of the regulations concerning industrial materials, the European Commission (EC) defines a "nanomaterial" based on its size, for the purpose of identifying materials for which special provisions might apply (e.g., for risk assessment or ingredient labeling). In particular, a nanomaterial is defined as "a natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm" [8].

Particle tracking analysis (PTA) has been previously used to determine the size of Brownian nanoparticles in colloidal suspensions [9–12], which are employed in industrial and biomedical applications. In the PTA method, the diffusion coefficients of targeted particles are first determined and then used to calculate the mean diameter of the particles based on the classical Stokes–Einstein relation. The application of the PTA method allows obtaining the number-based size distribution of the particles. The method can thus be used to establish whether a material falls under the EC definition of nanomaterial. Dynamic light scattering (DLS) can also be used to calculate the size of colloidal particles using the classical Stokes–Einstein equation, even though in this case the result is a light-scattering intensity-based mean size. When some additional information (e.g., size distribution, sphere structure) is available, one can calculate the corresponding number-based mean size from the DLS estimate; however, the reliability of the number-based size obtained from the DLS data is low. Consequently, PTA is more reliable than DLS for determining the number-based mean particle size. In order to calculate the mean size using the Stokes–Einstein relation, the PTA method analyzes the particle diffusion phenomena in one or two dimensions, in contrast to DLS, which is based on a three-dimensional analysis. This highlights one of the disadvantages of PTA compared with DLS: the smaller amount of information that can be obtained on the particle diffusion phenomenon.

Particles undergo different types of displacements in a colloidal particle suspension, for example diffusion and gravitational sedimentation. As DLS measures the sum of the different displacements, it does not allow distinguishing the individual movements. On the other hand, PTA can distinguish the different particle movements and thus allows their individual analysis. In this study, we analyzed the particle motion both in the direction of the gravitational force and in the direction perpendicular to it, to investigate the effect of gravitational sedimentation on the accuracy of the particle size determined by PTA. Although

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theoretical equations describing these effects are available, i.e., the Stokes-Einstein equation for particle diffusion and the Stokes equation for the sedimentation phenomenon, to our knowledge, the effect of the gravitational sedimentation of nano- to microsized particles on the particle size determined by PTA has not been directly assessed before. Although the shape of the particles affects their buoyancy, the effect of gravitational sedimentation on the accuracy of PTA-determined particle sizes is expected to depend on both the size and density of the particles; therefore, we examined spherical particles of four different sizes and four different materials. Spherical particles were used in this study to facilitate the comparison of the experimental results with the theoretical estimates. In particular, we employed a novel 2D-PTA approach to simultaneously determine the particle size and their density.

In addition, commercial apparatuses used in methods based on the Stokes–Einstein relation measure the mean size of a mixture of materials, but cannot identify the individual material types. Since some industrial components contain different materials, the simultaneous identification of each material and of the corresponding mean particle size and distribution by PTA represents a very attractive target. Although techniques such as field-flow fractionation with multi-angle light scattering and inductively coupled plasma mass spectrometry (FFF-MALS-ICP-MS) [13] and single-particle ICP-MS (sp-ICP-MS) [14] can assess both particle size and material types at the same time, the FFF-MALS-ICP-MS approach is rather expensive and requires larger samples. On the other hand, the sp-ICP-MS method has a limited detection size (e.g., 100 nm in the case of gold particles); hence, a more cost-effective method is required. Compared to the above methods, the PTA approach is less expensive, smaller size, and involves a measurement time of only a few minutes. In addition, particle suspensions sometimes contain air bubbles [15], whose presence reduces the reliability of size measurements performed by DLS, FFF-MALS-ICP-MS, and sp-ICP-MS methods, since they cannot distinguish the air bubbles. Therefore, in this study, we investigated a novel 2D-PTA method that can distinguish between different materials through the simultaneous observation of the diffusion and gravitational sedimentation of spherical particles.

2. Experimental section

2.1. Samples

The particle suspensions investigated in this study are summarized in Table 1. Surfactant-free aqueous dispersions of polystyrene (PS) latex, silica, silver, and gold particles were purchased and diluted with ultrapure water prepared using the Puric-ω system (Organo, Tokyo, Japan) with 0.1 μm filters. The measured mass concentration of the suspensions was approximately 0.001 mg/mL.

2.2. 2D-particle tracking analysis system

Fig. 1 illustrates the 2D-PTA system employed in this study. The system was equipped with a 30 mW semiconductor laser with a wavelength of 650 nm. A quartz cell with dimensions 28 mm (x direction) × 10 mm (y direction) × 1 mm (z direction) was employed in the measurements. The particle suspensions were injected from the top of the cell and the measurements were started after gravity sedimentation. In order to observe nano- to submicron-sized particles by an objective lens (×10) and a charge-coupled device (CCD) image sensor, the sample cell was irradiated from the side (y direction) by a laser and the light scattering from individual particles was observed as bright spots along the z direction by the CCD image sensor. The number of effective pixels in the CCD image sensor was 640 × 480. The pixel size was calibrated to 973 nm by manufacturer and the observable volume for this system was approximately 600 μm × 500 μm at the center of the cell, indicating the absence of wall effects on the particle movements. The ZEECOM software (Microtec Co., Ltd., Japan) was used to measure the displacement of the bright spots, as represented by the root mean square distance (MSD) per second covered along the x and y directions: MSD_X and MSD_Y represent the MSD in the x and y direction, respectively. The individual displacements were separated into two components, perpendicular (x) and parallel (y) to the direction of the gravitational force. The light scattering from the individual particles was captured at a frame rate of 1 fps with a CCD shutter speed of 1/60 s. More than 500 particles were observed during each measurement and the results presented in this study were averaged over all particles.

3. Results and discussion

Our study was based on the simultaneous analysis of two different types of particle movements, by combining light scattering data from the individual particles with common PTA measurements. Fig. 2 shows the particles suspended in a liquid phase and illustrates their individual movements. The particle movements were separated into two components, in the directions perpendicular (x) and parallel (y) to the gravitational force. The Brownian diffusion motion can randomly

Table 1
Characteristics of the particles investigated in this study.

Sample name	Material	Commercial name	Supplier	Diameter[a] [nm]	Density [g cm^{-3}]
PSL70		STADEX SC-0070-D	JSR Co.	70	1.06
PSL100		STADEX SC-0100-D	JSR Co.	100	1.06
PSL200		STADEX SC-024-S	JSR Co.	202	1.06
PSL300	Polystyrene latex	STADEX SC-032-S	JSR Co.	309	1.05
PSL500		G001	Fujikura Kasei Co.	509	1.05
PSL800		STADEX SC-081-S	JSR Co.	814	1.07
PSL1000		STADEX SC-103-S	JSR Co.	1005	1.05
Silica100		Silica Microspheres, Cat#24041	Polysciences, Inc	100	2.2
Silica300		Silica Microspheres, Cat#24321	Polysciences, Inc. micromod	300	2.2
Silica500	Silica	Sicastar: 502	Partikeltechnologie GmbH micromod	500	2.2
Silica800		Sicastar: 802	Partikeltechnologie GmbH micromod	800	2.2
Silica1000		Sicastar: 103	Partikeltechnologie GmbH micromod	1200	2.2
Silica1500		Sicastar: 153	Partikeltechnologie GmbH	1600	2.2
Silver50		50 nm Citrate BioPure Silver	nanoComposix, Inc.	52	10.5
Silver70	Silver	70 nm Citrate BioPure Silver	nanoComposix, Inc.	73	10.5
Silver100		100 nm Citrate BioPure Silver	nanoComposix, Inc.	94	10.5
Silver200		200 nm Citrate BioPure Silver	Sigma-Aldrich	194	10.5
Gold50		50 nm Citrate BioPure Gold	nanoComposix, Inc.	51	19.3
Gold70		70 nm Citrate BioPure Gold	nanoComposix, Inc.	74	19.3
Gold100	Gold	100 nm Citrate BioPure Gold	nanoComposix, Inc.	97	19.3
Gold200		200 nm Citrate BioPure Gold Concentrated Accurate	nanoComposix, Inc.	210	19.3
Gold400		Spherical Gold Nanoparticles, A11C-100- NPC	Sigma-Aldrich	400	19.3

[a] The diameter values were determined by dynamic light scattering (DLS) or transmission electron microscopy (TEM) by the respective suppliers.