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Measurements of effective sizes and diffusivities of nano-colloids and micro-particles

Jaeweon Cho [a,*], Young-Jun Park [b,1], Hyang Sun [c], Suhan Kim [a], Yeomin Yoon [d]

[a] *Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea*
[b] *Surface Technology Research Group, POSCO Technical Research Laboratories 699, Gumho-dong, Gwangyang, Jeonnam 545-090, Republic of Korea*
[c] *Biotechnology and Environment Standard Division, Agency for Technology and Standards, MOCIE, 2 Junang-dong, Gwachon, Gyeonggi 427-716, Republic of Korea*
[d] *Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA*

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Abstract

A theoretical diffusivity equation was proposed by Einstein [A. Einstein, Investigations of the Theory of the Brownian Movement, Dover Publication Inc., New York, 1956]; thermodynamic and drag (i.e., resistance or mobility relation) forces were compared at equilibrium. The diffusivity relationship, the ratio of the thermodynamic and drag forces, was combined with steady-state convection and diffusion equations to finally give a relationship between the retention times from flow field-flow fractionation (fl-FFF) and the diffusivity of a particle. An asymmetric fl-FFF system equipped with a regenerated cellulose membrane with molecular weight cutoff of 1000 and a micro channel employing both laminar channel and cross flows, was used to obtain chromatograms, using UV detection. A wide range of nano-colloids and micro-particles were measured with respect to their effective sizes and diffusivities. The classical FFF theory was incorporated with two different diffusion estimation relations: the Brownian and shear-induced diffusivities. It was found that the fl-FFF system provided similar and much lower sizes compared to absolute sizes provided by the manufacturer, for the smaller colloids (30, 60 nm), and the larger nano-colloids (90 nm and 0.2, 0.3, 0.43 and 0.5 μm) and micro-particles (0.5, 0.701, 0.993, 2, 3.1, and 8 μm), respectively. This was due to the larger nano-colloids and micro-particles being influenced by both the Brownian (the normal FFF mode) and shear-induced (the hyperlayer FFF mode) diffusions under the channel laminar and crossing flows condition within the micro channel of the fl-FFF system, which provided effective colloids and particles sizes. For all the nano-colloids and micro-particles, the fl-FFF system was able to determine the effective diffusion coefficients, irrespective of their size. For the micro-particles, the dimensionless diffusion coefficient was suggested to depend on the particle size, rather than that obtained by different methods suggested in previous works [E.C. Eckstein, D.G. Bailey, A.H. Shapiro, Self-diffusion of particles in shear flow of a suspension, J. Fluid Mech. 79 (Part 1) (1977) 191–208; D. Leighton, A. Acrivos, Measurement of shear-induced self-diffusion in concentrated suspensions of spheres, J. Fluid Mech. 177 (1987) 109–131].

Keywords: Effective size; Diffusivity; Nano-colloids; Micro-particles; Flow field-flow fractionation

1. Background and related theories

Diffusion is one of the most important factors influencing particles (including colloids) transport, including cake formation and transmission through membrane pores. It is obvious that particles (or colloids) with a higher diffusivity should have a lesser propensity for cake fouling. The only problem now remaining is how to determine the diffusivity of either particles or colloids: i.e., Brownian [1] versus shear-induced one [10,3,4] Wiesner and Chellam [5] also pointed out that the diffusivity of particles is a function of the particle size and has a minimum value around 0.1 μm; i.e., for particle size ranges lower and higher than approximately 0.1 μm, the particle diffusivity increases with decreasing size, but increases with increasing Brownian and

* Corresponding author. Tel.: +82 62 970 2443; fax: +82 62 970 2434.
E-mail address: jwcho@gist.ac.kr (J. Cho).
[1] Tel.: +82 61 790 9395; fax: 82 61 790 8801.

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shear-induced diffusivities, respectively. Attempts have been made to experimentally measure the shear-induced diffusivity using a rheometer equipped with a couette device [2,3]. According to these works, the shear-induced diffusion coefficient was expressed by the equation, $D = D'\gamma a^2$ (here, D is the diffusion coefficient, D' the dimensionless diffusion coefficient, γ the shear rate, and a the particle radius). When micro-sized particles (with diameter higher than approximately 400 μm) were used, the dimensionless diffusion coefficient was described as a function of the particle concentration, which ranged from 0.01 to 0.05 for diluted particle suspension. However, the shear-induced diffusivity of smaller particles (i.e., 0.5–8 μm) may not be easy to measure using the methods employing a couette device and optical detection. Both the Brownian and shear-induced diffusivities of particles and colloids can be measured using the normal and hyperlayer flow filed-flow fractionation (fl-FFF) modes, which employs two crossing flows (channel laminar and cross flows), a micro channel, and an accumulation membrane wall [6,7]. Dulog and Schauer (1996) [6] identified transition of particle size, a boundary between the normal (Brownian dominant region) and the hyperlayer (shear-induced diffusion dominant region) modes, having a minimum diffusivity determined using both symmetric and asymmetric flow FFF: 0.6 μm and 1.2–1.3 μm from symmetric and asymmetric flow FFF, respectively. Silica particles governed by the hyperlayer mode of flow FFF were rigorously investigated with different size calculating methods and fractionating analysis [8]. The schematic of the fl-FFF system is described in Fig. 1.

Theories for the fl-FFF system, in terms of the retention parameter (λ), channel geometries (channel thickness w (=250 μm), channel volume V^0), volumetric rate of crossflow (V_c), peak times ratio (R) and particle diffusivity (D), can be described as follows [9,7]:

$$\lambda = \frac{V^0 D}{V_c w^2} \tag{1}$$

$$R = 6\lambda\left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda\right] \tag{2}$$

where $R = t_0/t_r$ and t_0 and t_r represent the retention times of the unretained (void) and retained peaks, respectively, obtained from the FFF system, using UV detection at 254 nm.

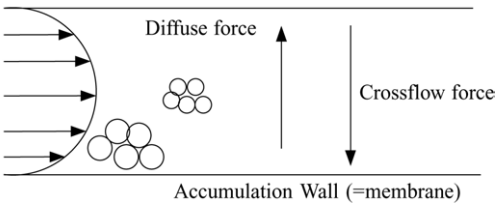

Fig. 1. Schematic of FFF system; there are two flows inside the micro channel of FFF, the first is channel laminar flow (direction to the right), and the second is crossflow (downward direction). Larger particle is more affected by the crossflow rather than smaller particle thus accumulated near the accumulation wall, while smaller particles can be toward the center of the channel and reach the exit more earlier. UV detector is placed at the right end side.

Equating Eqs. (1) and (2) gives Eq. (3), which can estimate the diffusivity (or size) of particles, as follows:

$$\lambda = \text{solution of Eq. (2)} = \frac{V^0 D}{V_c W^2} \tag{3}$$

Here the diffusivity can be substituted in two ways: either Brownian diffusivity (Eqs. (4) and (5)) [1] or shear-induced diffusivity (Eqs. (6) and (7)) [3,10,4]

$$D = \frac{kT}{6\pi\mu a} \tag{4}$$

$$\lambda = \text{solution of Eq. (2)} = \frac{V^0}{V_c w^2}\frac{kT}{6\pi\mu a} \tag{5}$$

for particles sizes of less than approximately 0.1 μm, according to [5]. Here k is the Boltzmann's constant, T the absolute temperature, μ the viscosity of fluid, and a is the particle radius.

When shear-induced diffusivity (Eq. (6)) is inserted in Eq. (3), Eq. (7) can be derived

$$D = D'\gamma a^2 \tag{6}$$

$$\lambda = \text{solution of Eq. (2)} = \frac{V^0}{V_c w^2} D'\gamma a^2 \tag{7}$$

Here D' and γ are the dimensionless diffusion coefficient and the shear rate, respectively, with $\gamma = 3Q/2BH_0^2$, where Q, B, and H_0 are the channel flow rate, the channel width, and the channel half height, respectively [4].

Eqs. (5) and (7) can be used to estimate the diffusivity (D) and dimensionless diffusion coefficient (D') for particles dominantly influenced by the Brownian and shear-induced diffusion, respectively.

2. Hypotheses

It is hypothesized that the diffusivities of particles or colloids with different sizes under different conditions can be determined using the fl-FFF system when the same flowing conditions are employed; i.e., the same flowing conditions are applied with the fl-FFF system but particles with different sizes are hypothesized to behave differently, which provides their different diffusivities. Similar to the notion suggested by [5], it is also hypothesized that there is a boundary particle size that imparts a minimum diffusivity.

3. Materials and methods

An asymmetric fl-FFF system (HRFFF 10.000 Series, Postnova, Germany) equipped with a regenerated cellulose membrane with molecular weight cutoff of 1000 (in standard molecular mass units) (Postnova, Art No. Z-MEM-AQU-005), and a micro-channel employing both laminar channel and cross flows (1.5 and 0.1 mL/min, respectively), was used to obtain chromatograms, using UV detection at 254 nm. An amount of 0.01% FL-70 (mixed with anionic and neutral surfactants) (Fisher Scientific, New Jersey, US) and 0.1 mM NaN_3 were used as the eluent. The wide range of colloids and particles used were