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, MOCTE, 2 Jimun-dong, Gyeonggi-do, Gyeonggi 427-716, Republic of Korea
d Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

Received 7 May 2005; received in revised form 9 August 2005; accepted 23 August 2005
Available online 14 October 2005

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].

© 2005 Elsevier B.V. All rights reserved.

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...
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, $D = D' \rho \gamma^2$ (here, $D$ is the diffusion coefficient, $D'$ the dimensionless diffusion coefficient, $\gamma$ the shear rate, and $\rho$ 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]. Dialog 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 ($\lambda$), channel geometries (channel thickness $w$ =250 µm), channel volume $V_c$, volumetric rate of crossflow ($V_c$), peak times ratio ($R$) and particle diffusivity ($D$), can be described as follows [9,7]:

$$\lambda = \frac{V_c \rho D}{V_c \rho w^2}$$  \hspace{1cm} (1)

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

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

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

$$\lambda = \text{solution of Eq. (2)} = \frac{V_c \rho D}{V_c \rho w^2}$$  \hspace{1cm} (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]

$$D = \frac{kT}{6 \pi \mu w}$$  \hspace{1cm} (4)

$$\lambda = \text{solution of Eq. (2)} = \frac{V_c \rho kT}{V_c \rho w^2}$$  \hspace{1cm} (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, $\mu$ the viscosity of fluid, and $w$ is the particle radius.

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

$$D = D' \rho \gamma^2$$  \hspace{1cm} (6)

$$\lambda = \text{solution of Eq. (2)} = \frac{V_c \rho D' \rho \gamma^2}{V_c \rho w^2}$$  \hspace{1cm} (7)

Here $D'$ and $\gamma$ are the dimensionless diffusion coefficient and the shear rate, respectively, with $\gamma = 3Q/2BH_{lf}$, where $Q, B, and H_{lf}$ 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 NaN3 were used as the eluent. The wide range of colloids and particles used were...
purchased from the Duke Scientific (US), and included latex microsphere suspension (30, 60 and 90 nm, and 0.2, 0.3, 0.43, 0.50, 0.82, 1.0, 2.0, 3.1, and 8.0 \mu m) and NIST traceable polymer microsphere (0.701 and 0.993 \mu m). The fl-FFF system was tested in two different modes: the normal and hyper modes, respectively [6,7,11,12].

4. Results and discussion

As shown in Fig. 2 (a) and (b), the peak times of the injected colloids and micro-particles increased and decreased, respectively, as their sizes increase, as their diffusivities decrease (see Eq. (4)) and increase (see Eq. (6)), respectively. Thus, it was verified that the diffusional behaviors of the nano-colloids (30 nm–0.5 \mu m) and micro-particles (0.5–8 \mu m) can be separated by the two crossing flows (i.e., laminar and cross flows) in the normal and hyper modes, respectively. The retention times of all the tested colloids and particles were plotted as a function of their size, as shown in Fig. 3. As hypothesized, two different diffusion trends were clearly found, supporting both the first and second hypotheses; the boundary particle size that imparted a minimum diffusivity was 0.5 \mu m, which was different to the approximately 0.1 and 1.2–1.3 \mu m, as suggested by [5] and [6], respectively.

Based on all the measurements from the fl-FFF system, the size and diffusivity of the nano-colloids, and the dimensionless diffusion coefficient and diffusivity of the micro-particles, are summarized in Table 1. For the first two nano-colloids (i.e., 30 and 60 nm), the sizes obtained using the fl-FFF system were similar to the colloids sizes provided by the manufacturer. However, the measured sizes of the other colloids (i.e., 90 nm–0.5 \mu m) were much lower than the corresponding sizes provided by the manufacturer. This was due to the influence of the shear-induced diffusivity, which increases with increasing colloid size, as previously described; the diffusion of both 30 and 60 nm colloids was mostly influenced by Brownian motion, but the larger colloids were influenced by both Brownian and shear-induced motions [4]. Thus, it should be noted that the measured values are not absolute but effective sizes for colloids affected by the two diffusions under the given flow conditions. Diffusion coefficients for the nano-colloids were also determined using the two different methods: the first employed the Stokes–Einstein equation (Eq. (4)), with the colloids size provided by the manufacturer, and the second used the fl-FFF system and FFF theory (i.e., Eq. (3)). As listed in Table 1, the two methods provided very different diffusivities. It is unknown which method gives the more appropriate values, although it should also be noted that the latter considered both the Brownian and shear-induced motions of the colloids under the laminar and crossing flows condition to provide the effective diffusivity.

The diffusion coefficients of the micro-particles (0.5–8.0 \mu m) were also measured, and are summarized in Table 1. As they are mostly influenced by shear-induced diffusion, the dimensionless diffusion coefficient ($\bar{D}$) was calculated using Eq. (7), ranging 0.001–0.045, which was somewhat different from the values provided by [2] and [3]. It should also be noted that
A wide range of nano-colloids and micro-particles were measured, with respect to their effective sizes and diffusivities, using the Fl-FFF system equipped with a regenerated cellulose membrane. The classical FFF theory was incorporated into two different diffusion estimation relations: the Brownian and shear-induced diffusivities. It was found that the Fl-FFF system was able to determine the effective diffusion coefficients, irrespective of their size. Lastly, for the micro-particles, the dimensionless diffusion coefficient was suggested to depend on the particle size, rather than to that obtained by the different methods suggested in previous works [2] and [3].

5. Conclusions

A wide range of nano-colloids and micro-particles were measured, with respect to their effective sizes and diffusivities, using the Fl-FFF system equipped with a regenerated cellulose membrane. The classical FFF theory was incorporated into 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 nm). This was due to the larger nano-colloids and micro-particles being influenced by both the Brownian and shear-induced diffusions under the laminar flow and crossing flow conditions within the micro channel of the Fl-FFF system, which provided the 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.

References


