



Nanoparticle diffusivity in narrow cylindrical pores



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ABSTRACT

The hydrodynamic force on particles increases significantly when the particle movement is in the vicinity of solid boundaries. The increased drag decreases the mobility of the particles close to the wall, and slows down the Brownian movement. Since the Brownian movement of particles is the cause of particle dispersion and diffusion, it follows that the diffusion of particles close to a wall is slower than the diffusion in an unbounded fluid. Using a Monte Carlo method, the isothermal Brownian dispersion of spherical nanoparticles close to the wall of narrow cylindrical pores is simulated in Newtonian, isothermal fluids and the cross-section averaged particle diffusion is calculated. The pore to particle radii ratio in these simulations is in the range $5 < R/\alpha < 140$ and the range of nanoparticle radii is $3 < \alpha < 100$ nm. It is observed that the effect of the pore walls is a significant reduction of the average particle diffusivity. The diffusivity reduction is strictly a geometric effect. It depends on the size of the particles and the pore-to-particle diameter ratio and does not depend on the fluid and particle thermodynamic and transport properties, such as relative density and fluid viscosity.

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1. Introduction

The mass transfer of micro- and nano-particles through narrow membrane pores is met in several physical processes ranging from nanoparticle separation and fractionation, to drug delivery, to measurements of nanofluid diffusivity. It is well-known that, when particles pass through narrow tubes, they experience a higher fluid drag, which is caused by the constraint of the boundaries of the flow. In such cases, the velocity of the particles is reduced, often-times significantly [1]. The velocity retardation, due to the proximity of boundaries, also applies to the Brownian movement, which is the physical mechanism for the diffusion of particles. The retardation of the Brownian movement causes decreased diffusivity in pores and this has been referred to in the past as “hindered transport” and “hindered diffusivity” [2,3].

In studying the dynamics of translocation of gold nanoparticles, Goyal et al. [4] observed experimentally that the average particle diffusivity decreased by a factor of five. While studying the electrophoretic migration of nanoparticles through membrane pores, Han et al. [5] also observed that the diffusivity of nanoparticles within the nano-pores decreased by a factor of 20–23. They attributed the dramatic decrease of nanoparticle diffusivity to an increase of the fluid viscosity inside the pores. Similarly, Lan and White [6] observed diffusion hindrance of nanoparticles in conical pores, when they applied a pressure-reversal technique to capture the nanoparticles. Several other researchers also observed the

slower motion of solid particles as well as of fluid macromolecules inside narrow tubes and membrane pores [7–10]. The slower movement of these particles has been attributed to electric charge interactions (for charged particles), and the increased fluid viscosity. Since nanoparticle diffusivity is a very important transport property for the movement and heat transfer of nanofluids [11] it is important to determine the changes of diffusivity because of the proximity of flow boundaries.

When the particles are very fine, the Brownian movement causes their axial and radial dispersion inside pores. The interactions of particles with the solid boundaries and the confinement of the fluid near the pore boundaries cause a higher hydrodynamic force on the particles, which shows as higher fluid drag and particle retardation. This phenomenon was first investigated by Faxen [12] who derived an analytical power-law solution for the hydrodynamic force of spherical particles within parallel planes. Happel and Brenner [13], among others, performed a more detailed analysis of the motion of spherical particles in the vicinity of solid boundaries and derived expressions for the hydrodynamic drag enhancement in the longitudinal and radial directions. Summaries of the analytical and experimental studies on the hydrodynamic interactions of spherical particles with solid and fluid boundaries are given in [1,14]. It is apparent in all these studies that the hydrodynamic drag on the spherical particles increases significantly when they approach a solid surface. A numerical study of the Brownian movement [15] used the results for the enhanced hydrodynamic drag to explain the retardation of spherical particles, driven by thermophoresis, close to a plane surface.

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The diffusivity of particles in fluids is the result of the Brownian movement, which is caused by the random and incessant movement of the fluid molecules. The so-called, Einstein-Stokes diffusivity [16] for spherical particles is given by the expression:

$$D_0 \equiv \frac{d}{dt} \left\langle \frac{\vec{x} \cdot \vec{x}}{2} \right\rangle = \frac{k_B T}{6\pi\alpha\mu_f}, \quad (1)$$

where k_B is the Boltzmann constant; T is the absolute temperature of the fluid; α is the radius of the particle; and μ_f is the dynamic viscosity of the fluid. The Einstein-Stokes diffusivity is a transport property of the fluid-particle system and has been derived for dilute systems of spherical particles in fluids [16]. The diffusivity of particles in dense systems is lesser and is a strong function of the volumetric concentration of the fluid-particle system.

In a Newtonian framework the random Brownian movement of the particles may be considered to be the action of a random body force, which continuously acts on the particles and affects their motion in a random way. It has been proven that the equivalent force, which causes the random movement of spherical particles of radius α and a magnitude of dispersion equal to the Stokes-Einstein diffusivity, is [17–19]:

$$\vec{F}_{Br} = \vec{R} \sqrt{\frac{12\pi k_B T \alpha \mu_f}{\Delta t}}, \quad (2)$$

where \vec{R} is a vector whose components are Gaussian random numbers with zero mean and unit standard deviation; and Δt is the time interval when the random force is applied on a particle. When the random force is integrated over a long period of time t ($t \gg \Delta t$) the results for D_0 are independent of the choice of the interval Δt and this continuous force yields the Stokes-Einstein diffusion coefficient of Eq. (1) [20,21]. In the continuum mechanics approach that is followed in this paper, the Brownian force acts continuously on the particles, while its magnitude changes at every step of the MC simulation following the vector with random components, \vec{R} . Given the choice of this vector, the time-average of the Brownian force is zero and the variance of the force is $12\pi\alpha k_B \mu_f / \Delta t$. It must be noted that one may follow an alternative stochastic approach and formulate the particle velocity and position equations as stochastic differential equations. This type of approach is often used for the study of macromolecule properties and polymeric fluids [21]. The continuum mechanics, discrete particle approach, which makes use of a Lagrangian equation for the particle motion, is favored in this paper, because it is simpler to formulate and easier to implement.

This study examines numerically the hydrodynamic effect of cylindrical pore walls on the Brownian movement of nanoparticles inside the pores, and the overall effect of the pore walls on the area-average diffusivity of the nanoparticles. The MC simulation method is used to determine the dispersion of a large ensemble of nanoparticles in narrow cylindrical tubes of various diameters, using the Lagrangian computations. Suitable time- and ensemble-averages enable us to determine the time-averaged local movement of the nanoparticles, their dispersion, the local particle diffusivity and the pore-averaged diffusivity. The hindered diffusion of particles is expressed as the dimensionless ratio of the actual diffusion to the diffusion of the same particle-fluid system in an infinite domain.

2. Increased drag due to a boundary

We consider a spherical nanoparticle of radius α immersed in a Newtonian fluid of density ρ_f and viscosity μ_f . The velocity of the fluid is denoted by u and that of the particle by v . For most Newtonian fluids the flow is Stokesian, ($Re_p \ll 1$, with

$Re_p = 2\alpha\rho_f(u - v)/\mu_f$). The system is isothermal, which implies that the fluid viscosity is uniform, and the thermophoretic force is zero. Because the system is dilute, the diffusiophoresis also vanishes. The fluid inside the pore is at rest and, therefore, the space- and time-averages of u vanish.

Under these conditions, the Lagrangian equation of motion of the particle becomes:

$$m_p \frac{d^2 \vec{x}}{dt^2} = \vec{R} \sqrt{\frac{12\pi k_B T \alpha \mu_f}{(\Delta t)}} - 6\pi f_{Kn} \alpha \mu_f \vec{v} K + m_p (\rho_p - \rho_f) \vec{g}, \quad (3)$$

where \vec{v} is the instantaneous velocity of the particles; f_{Kn} is a correction factor that accounts for the slip at the solid liquid interface that depends on the Knudsen number and is similar to Cunningham's factor; the last term represents the gravitational force on the particle; and K is the hydrodynamic drag enhancement coefficient because of the proximity to the solid boundary [12,13,15]. Given that the fluids considered here are liquids, the mean free path of the fluid is very low in comparison to the radii of the nanoparticles considered in this study. Hence, $Kn \ll 1$ and $f_{Kn} \approx 1$. For nanoparticles, the gravitational force is proportional to α^3 , several orders of magnitude less than the other terms of Eq. (3), and is usually neglected in the Lagrangian simulations [22,23,16].

Fig. 1 depicts the geometrical setting of the problem. The particle of radius α is located at a distance h from the wall of the cylinder, whose radius is R . The length of the cylinder, L , is much greater than the radius R , so the particle is inside the cylinder for the entire duration of the Lagrangian simulation. The coordinate system (r, z) is also shown in the Figure. Because the fluid hydrodynamics associated with the movement of the particle are different when the particle translates perpendicular or parallel to the wall, the drag enhancement coefficient, K , has components that are different in the two directions, r and z . Happel and Brenner [13] provide an analytical expression for the component K_z , which is pertinent to the translation of the sphere parallel to the wall:

$$K_z = 1 + \frac{9\alpha}{16h}. \quad (4)$$

For the movement of the sphere perpendicular to the wall, Happel and Brenner [13] give the values of the pertinent drag enhancement coefficient in a tabular form. Based on these values a correlation was developed to be used in the Lagrangian computations:

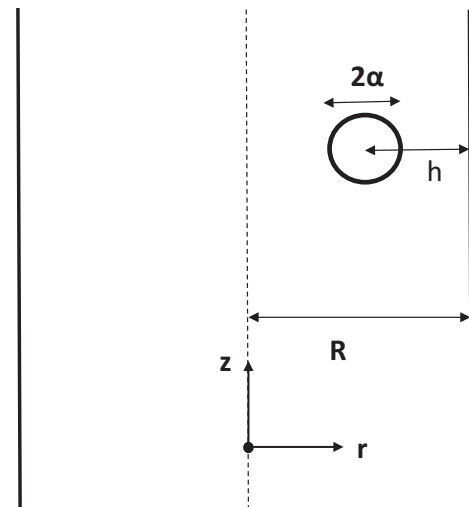


Fig. 1. A particle of radius α , translating in a cylinder of radius R at a distance h from the wall.

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